

(2 Sep 03)

Section 2 - Input Description

This section of the manual describes the input to GAMESS. The section is written in a reference, rather than tutorial fashion. However, there are frequent reminders that more information can be found on a particular input group, or type of calculation, in the 'Further Information' section of this manual. There are also a number of examples shown in the 'Input Examples' section.

The order of this section is chosen to approximate the order in which most people prepare their input (\$CONTRL, \$BASIS/\$DATA, \$GUESS, and so on). The next page contains a list of all possible input groups, in the order in which they can be found in this section.

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<u>name</u>	<u>function</u>	<u>module:routine*</u>
Molecule, basis, wavefunction specification:		
\$CONTRL	chemical control data	INPUTA: START
\$SYSTEM	computer related control data	INPUTA: START
\$BASIS	basis set	INPUTB: BASIS
\$DATA	molecule, basis set	INPUTB: MOLE
\$ZMAT	coded z-matrix	ZMATRX: ZMATIN
\$LIBE	linear bend data	ZMATRX: LIBE
\$SCF	HF-SCF wavefunction control	SCFLIB: SCFIN
\$SCFMI	SCF-MI input control data	SCFMI :MIINP
\$DFT	density functional input	DFT :DFTINP
\$MP2	2nd order Moller-Plesset	MP2: MP2INP
\$CIS	singly excited CI	CISGRD:CISINP
\$CISVEC	vectors for CIS	CISGRD:CISVRD
\$CCINP	coupled cluster input	CCSDT: CCINP
\$GUESS	initial orbital selection	GUESS: GUESMO
\$VEC	orbitals (formatted)	GUESS: READMO
\$MOFRZ	freezes MOs during SCF runs	EFPCOV:MFRZIN
Potential energy surface options:		
\$STATPT	geometry search control	STATPT: SETSIG
\$TRUDGE	nongradient optimization	TRUDGE: TRUINP
\$TRURST	restart data for TRUDGE	TRUDGE: TRUDGX
\$FORCE	hessian, normal coordinates	HESS: HESSX
\$CPHF	coupled-Hartree-Fock options	CPHF: CPINP
\$HESS	force constant matrix (formatted)	HESS: FCMIN
\$GRAD	gradient vector (formatted)	HESS: EGIN
\$DIPDR	dipole deriv. matrix (formatted)	HESS: DDMIN
\$VIB	HESSIAN restart data (formatted)	HESS: HSSNUM
\$MASS	isotope selection	VIBANL:RAMS
\$IRC	intrinsic reaction path	RXNCRD:IRCX
\$VSCF	vibrational SCF and MP2	VSCF :VSCFIN
\$VIBSCF	VSCF restart data (formatted)	VSCF :VGRID
\$DRC	dynamic reaction path	DRC: DRCDRV
\$GLOBOP	Monte Carlo global optimization	GLOBOP:GLOPDR
\$GRADEX	gradient extremal path	GRADEX:GRXSET
\$SURF	potential surface scan	SURF :SRFINP
Interpretation, properties:		
\$LOCAL	orbital localization control	LOCAL: LMOINP
\$TWOEI	J,K integrals (formatted)	LOCCD: TWEIIN
\$TRUNCN	localized orbital truncations	EFPCOV:TRNCIN
\$ELMOM	electrostatic moments	PRPLIB: INPELM
\$ELPOT	electrostatic potential	PRPLIB: INPELP
\$ELDENS	electron density	PRPLIB: INPELD
\$ELFLDG	electric field/gradient	PRPLIB: INPELF
\$POINTS	property calculation points	PRPLIB: INPPGS
\$GRID	property calculation mesh	PRPLIB: INPPGS
\$PDC	MEP fitting mesh	PRPLIB: INPPDC
\$MOLGRF	orbital plots	PARLEY:PLTMEM
\$STONE	distributed multipole analysis	PRRPOP: STNRD
\$RAMAN	Raman intensity	RAMAN :RAMANX
\$ALPDR	alpha polar. der. (Formatted)	RAMAN :ADMIN
\$MOROKM	Morokuma energy decomposition	MOROKM:MOROIN

\$FFCALC finite electric field
\$TDHF time dependent HF NLO properties

FFIELD: FFLDX
TDHF: TDHFX

Solvation models:

\$EFRAG effective fragment potentials
\$FRAGNAME specific named fragment pot.
\$FRGRPL inter-fragment repulsion
\$PRTEFP simplified EFP generation
\$DAMP EFP multipole screening fit
\$DAMPGS initial guess screening params
\$PCM polarizable continuum model
\$PCMGRD PCM gradient contrl
\$PCMCAV PCM cavity generation
\$TESCAV PCM cavity tessellation
\$NEWCAV PCM escaped charge cavity
\$IEFPCM PCM integral equation form. data
\$PCMITR PCM iterative IEF input
\$DISBS PCM dispersion basis set
\$DISREP PCM dispersion/repulsion
\$COSGMS conductor-like screening model
\$SCRf self consistent reaction field

EFINP:EFINP
EFINP:RDSTFR
EFINP:RDDFRL
EFINP :PREFIN
CHGPEN:CGPINP
CHGPEN:CGPINP
PCM :PCMINP
PCMCV2:PCMGIN
PCM :MAKCAV
PCMCV2:TESIN
PCM :DISREP
PCM :IEFDAT
PCMIEF:ITIEFIN
PCMDIS:ENLBS
PCMVCH:MORETS
COSMO :COSMIN
SCRf:ZRFINP

Integral and integral modification options:

\$ECP effective core potentials
\$MCP model core potentials
\$RELWFN relativistic correction
\$EFIELD external electric field
\$INTGRL format for 2e- integrals
\$FMM fast multipole method
\$TRANS integral transformation

ECPLIB:ECPPAR
MCPINP:MMPRED
INPUTB:RWFINP
PRPLIB:INPEF
INPUTA:START
QMFM :QFMMIN
TRFIN :TRANS

MCSCF and CI wavefunctions, and their properties:

\$CIINP control over CI calculation
\$DET determinant full CI for MCSCF
\$CIDET determinant full CI
\$GEN determinant general CI for MCSCF
\$CIGEN determinant general CI
\$ORMAS occ. restricted mult. act. sp.
\$GCILST general determinant list
\$SODET second order determinant CI
\$DRT distinct row table for MCSCF
\$CIDRT distinct row table for CI
\$MCSCF parameters for MCSCF
\$MCQDPT multireference pert. Theory
\$CISORT integral sorting
\$GUGEM Hamiltonian matrix formation
\$GUGDIA Hamiltonian eigenvalues/vectors
\$GUGDM 1e- density matrix
\$GUGDM2 2e- density matrix
\$LAGRAN CI lagrangian matrix
\$TRFDM2 2e- density backtransformation
\$TRANST transition moments, spin-orbit

GAMESS:WFNCI
ALDECI:DETINP
ALDECI:DETINP
ALGNCI:GCIINP
ALGNCI:GCIINP
ORMAS :FCINPT
ALGNCI:GCIGEN
FSODCI:SOCINP
GUGDRT:ORDORB
GUGDRT:ORDORB
MCSCF :MCSCF
MCQDPT:MQREAD
GUGSRT:GUGSRT
GUGEM :GUGAEM
GUGDGA:GUGADG
GUGDM :GUGADM
GUGDM2:GUG2DM
LAGRAN:CILGRN
TRFDM2:TRF2DM
TRNSTN:TRNSTX

* this column is more useful to programmers than to users.

\$CONTRL group (optional)

This is a free format group specifying global switches.

SCFTYP		specifies the self-consistent field the wavefunction. You may choose from:
= RHF		Restricted Hartree Fock calculation (default)
= UHF		Unrestricted Hartree Fock calculation
= ROHF		Restricted open shell Hartree-Fock. (high spin, see GVB for low spin)
= GVB		Generalized valence bond wavefunction or OCBSE type ROHF. (needs \$SCF input)
= MCSCF		Multiconfigurational SCF wavefunction (this requires \$DET or \$DRT input)
= NONE		indicates a single point computation, rereading a converged SCF function. This option requires that you select CITYP=ALDET, ORMAS, FSOCI, GENCI, or GUGA, requesting only RUNTYP=ENERGY or TRANSITN, and using GUESS=MOREAD.

The treatment of electron correlation for the above SCF wavefunctions is controlled by the keywords MPLEVL, CITYP, and CCTYP contained in this group, or DFTTYP which is given in \$DFT. Obviously, at most one of MPLEVL, CITYP, CCTYP, or DFTTYP may be chosen in any given run.

MPLEVL	=	chooses Moller-Plesset perturbation theory level, after the SCF. See \$MP2 and \$MCQDPT input groups.
	= 0	skip the MP computation (default)
	= 2	perform second order energy correction.

MP2 (aka MBPT(2)) is only implemented for RHF, UHF, ROHF, and MCSCF wavefunctions. Gradients are available for RHF and UHF, so for the others you may choose a RUNTYP of ENERGY, TRUDGE, SURFACE, or FFIELD only.

CITYP	=	chooses CI computation after the SCF, for any SCFTYP except UHF.
	= NONE	skips the CI. (default)
	= CIS	single excitations from a SCFTYP=RHF reference, only. This is for the treatment of excited states, with analytic nuclear gradients available. See the \$CIS input group.
	= ALDET	runs the Ames Laboratory determinant full CI package, requiring \$CIDET input. Use with RUNTYP=ENERGY only.
	= ORMAS	runs an Occupation Restricted Multiple Active Space determinant CI. The input is \$CIDET and \$ORMAS.
	= FSOCI	runs a full second order CI using determinants, with RUNTYP=ENERGY only. The input is \$CIDET and \$SODET.
	= GENCI	runs a determinant CI program that permits arbitrary specification of the determinants, requiring \$CIGEN input. Use with RUNTYP=ENERGY only.
	= GUGA	runs the Unitary Group CI package, which requires \$CIDRT input. Gradients are available only for RHF, so for other SCFTYPs, you may choose only RUNTYP=ENERGY, TRUDGE, SURFACE, FFIELD, TRANSITN.

CCTYP	chooses a Coupled-Cluster computation after SCF, available for SCFTYP=RHF. See also the \$CCINP group.
= NONE	skips CC computation (default).
= LCCD	perform a coupled-cluster calculation using the linearized coupled-cluster method with double excitations.
= CCD	perform a CC calculation using the coupled-cluster method with double excitations.
= CCSD	perform a CC calculation using the coupled-cluster method with single and double excitations.
= CCSD(T)	in addition to the CCSD run, the non-iterative triples corrections are calculated to give the standard CCSD[T] and CCSD(T) energies.
= R-CC	in addition to standard CCSD, CCSD[T], and CCSD(T) calculations, renormalized R-CCSD[T] and R-CCSD(T) calculations are performed. The cost of the renormalized calculations equals standard CCSD(T).
= CR-CC	in addition to CCSD, CCSD[T], CCSD(T), R-CCSD[T], and R-CCSD(T) calculations, the completely renormalized CR-CCSD[T] and CR-CCSD(T) energies are computed. The cost of CR-CCSD[T] and CR-CCSD(T) calculations, in their noniterative triples corrections portion, is twice the standard [T] and (T) corrections.

The most reasonable choices are CCSD, CCSD(T), or CR-CC.

Analytic gradients are not available, so use CCTYP only for RUNTYP=ENERGY, TRUDGE, SURFACE, or maybe FFIELD.

Any publication describing the results of CC calculations obtained using GAMESS should give reference to

P. Piecuch, S.A. Kucharski, K. Kowalski, and M. Musial, Comput.Phys. Commun., 149, 71-96, 2002

For more information about the R-CCSD(T) and CR-CCSD(T) methods, see Section 4, 'Further Information'.

RUNTYP specifies the type of computation, for example at a single geometry point:

= ENERGY	Molecular energy. (default)
= GRADIENT	Molecular energy plus gradient.
= HESSIAN	Molecular energy plus gradient plus second derivatives, including harmonic vibrational analysis. See the \$FORCE input group.

multiple geometry options:

= OPTIMIZE	Optimize the molecular geometry using analytic energy gradients. See \$STATPT.
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- = TRUDGE Non-gradient total energy minimization. See groups \$TRUDGE and \$TRURST.
- = SADPOINT Locate saddle point (transition state). See the \$STATPT group.
- = IRC Follow intrinsic reaction coordinate. See the \$IRC group.
- = VSCF Compute anharmonic vibrational corrections (see \$VSCF)
- = DRC Follow dynamic reaction coordinate. See the \$DRC group.
- = GLOBOP global optimization of effective fragment positions via Monte Carlo. See \$GLOBOP.
- = GRADEXTR Trace gradient extremal. See the \$GRADEX group.
- = SURFACE Scan linear cross sections of the potential energy surface. See \$SURF.

single geometry property options:

- = PROP Properties will be calculated. A \$DATA deck and converged \$VEC group should be input. Optionally, orbital localization can be done. See \$ELPOT, etc.
- = MOROKUMA Performs monomer energy decomposition. See the \$MOROKM group.
- = TRANSITN Compute radiative transition moment or spin-orbit coupling. See \$TRANST group.
- = FFIELD applies finite electric fields, most commonly to extract polarizabilities. See the \$FFCALC group.
- = TDHF analytic computation of time dependent polarizabilities. See the \$TDHF group.
- = MAKEFP creates an effective fragment potential.

* * * * *

Note that RUNTYPs which require the nuclear gradient are
GRADIENT, HESSIAN, OPTIMIZE, SADPOINT,
GLOBOP, IRC, GRADEXTR, and DRC

These may not be used for any CI, MP2, or CC calculation
unless the gradient can be computed, as indicated above.

* * * * *

-
- EXETYP = RUN Actually do the run. (default)
 - = CHECK Wavefunction and energy will not be evaluated. This lets you speedily check input and memory requirements. See the overview section for details.
Note that you must set PARALL=.TRUE. in \$SYSTEM to test distributed memory allocations.
 - = DEBUG Massive amounts of output are printed, useful only if you hate trees.
 - = routine Maximum output is generated by the routine named. Check the source for the routines this applies to.
- MAXIT = Maximum number of SCF iteration cycles. Pertains only to RHF, UHF, ROHF, or GVB runs. See also MAXIT in \$MCSF. (default = 30)

\$CONTRL

ICHARG = Molecular charge. (default=0, neutral)

MULT = Multiplicity of the electronic state
 = 1 singlet (default)
 = 2,3,... doublet, triplet, and so on.

ICHARG and MULT are used directly for RHF, UHF, ROHF.
 For GVB, these are implicit in the \$SCF input, while for
 MCSCF or CI, these are implicit in \$DRT/\$CIDRT or
 \$DET/\$CIDET input. You must still give them correctly
 here.

ECP = effective core potential control.
 = NONE all electron calculation (default).
 = READ read the potentials in \$ECP group.
 = SBKJC use Stevens, Basch, Krauss, Jasien, Cundari potentials for
 all heavy atoms (Li-Rn are available).
 = HW use Hay, Wadt potentials for all the heavy atoms (Na-Xe
 are available).
 = MCP use Huzinaga's Model Core Potentials. Gradients are not
 available, and see the \$MCP group for how to input these.

RELWFN = NONE (default) See also \$RELWFN input group.
 = NESC normalised elimination of small component, the method of
 K. Dyall
 = RESC relativistic elimination of small component, the method of
 T. Nakajima and K. Hirao.

* * * the next three control molecular geometry * * *

COORD = choice for molecular geometry in \$DATA.
 = UNIQUE only the symmetry unique atoms will be given, in
 Cartesian coords (default).
 = HINT only the symmetry unique atoms will be given, in
 Hilderbrandt style internals.
 = CART Cartesian coordinates will be input. Please read the
 warning just below!!!
 = ZMT GAUSSIAN style internals will be input.
 = ZMTMPC MOPAC style internals will be input.
 = FRAGONLY means no part of the system is treated by ab initio means,
 hence \$DATA is not given. The system is specified by
 \$EFRAG.

Note that the CART, ZMT, ZMTMPC choices require input of all atoms in the molecule.
 These three also orient the molecule, and then determine which atoms are unique. The
 reorientation is very likely to change the order of the atoms from what you input. When the
 point group contains a 3-fold or higher rotation axis, the degenerate moments of inertia often
 cause problems choosing correct symmetry unique axes, in which case you must use

COORD=UNIQUE rather than Z-matrices.

Warning: The reorientation into principal axes is done only for atomic coordinates, and is not applied to the axis dependent data in the following groups: \$VEC, \$HESS, \$GRAD, \$DIPDR, \$VIB, nor Cartesian coords of effective fragments in \$EFrag. COORD=UNIQUE avoids reorientation, and thus is the safest way to read these.

Note that the choices CART, ZMT, ZMTMPC require the use of a \$BASIS group to define the basis set. The first two choices might or might not use \$BASIS, as you wish.

UNITS	=	distance units, any angles must be in degrees.
	=	ANGS Angstroms (default)
	=	BOHR Bohr atomic units
NZVAR	=	0 Use Cartesian coordinates (default).
	=	M If COORD=ZMT or ZMTMPC and a \$ZMAT is not given: the internal coordinates will be those defining the molecule in \$DATA. In this case, \$DATA must not contain any dummy atoms. M is usually 3N-6, or 3N-5 for linear.
	=	M For other COORD choices, or if \$ZMAT is given: the internal coordinates will be those defined in \$ZMAT. This allows the use of more sophisticated internal coordinate choices. M is ordinarily 3N-6 (3N-5), unless \$ZMAT has linear bends.

NZVAR refers mainly to the coordinates used by OPTIMIZE or SADPOINT runs, but may also print the internal's values for other run types. You can use internals to define the molecule, but Cartesians during optimizations!

LOCAL	=	controls orbital localization.
	=	NONE Skip localization (default).
	=	BOYS Do Foster-Boys localization.
	=	RUEDNBRG Do Edmiston-Ruedenberg localization.
	=	POP Do Pipek-Mezey population localization.
		See the \$LOCAL group. Localization does not work for SCFTYP=GVB or CITYP.
ISPHER	=	Spherical Harmonics option
	=	-1 Use Cartesian basis functions to construct symmetry adapted linear combination (SALC) of basis functions. The SALC space is the linear variation space used. (default)
	=	0 Use spherical harmonic functions to create SALC functions, which are then expressed in terms of Cartesian functions. The contaminants are not dropped, hence this option has EXACTLY the same variational space as ISPHER=-1. The only benefit to obtain from this is a population analysis in terms of pure s,p,d,f,g functions.
	=	+1 Same as ISPHER=0, but the function space is truncated to eliminate all contaminant Cartesian functions [3S(D), 3P(F), 4S(G), and 3D(G)] before constructing the SALC functions. The computation corresponds to the use of a spherical harmonic basis.

QMTTOL = linear dependence threshold
 Any functions in the SALC variational space whose eigenvalue of the overlap matrix is below this tolerance is considered to be linearly dependent. Such functions are dropped from the variational space. What is dropped is not individual basis functions, but rather some linear combination(s) of the entire basis set that represent the linear dependent part of the function space. The default is a reasonable value for most purposes, 1.0E-6.

When many diffuse functions are used, it is common to see the program drop some combinations. On occasion, in multi-ring molecules, we have raised QMTTOL to 3.0E-6 to obtain SCF convergence, at the cost of some energy.

* * * interfaces to other programs * * *

MOLPLT = flag that produces an input deck for a molecule drawing program distributed with GAMESS. (default is .FALSE.)

PLTORB = flag that produces an input deck for an orbital plotting program distributed with GAMESS. (default is .FALSE.)

AIMPAC = flag to create an input deck for Bader's Atoms In Molecules properties code. (default=.FALSE.) For information about this program, see the URL <http://www.chemistry.mcmaster.ca/faculty/bader/aim>

FRIEND = string to prepare input to other quantum programs, choose from
 = HONDO for HONDO 8.2
 = MELDF for MELDF
 = GAMESSUK for GAMESS (UK Daresbury version)
 = GAUSSIAN for Gaussian 9x
 = ALL for all of the above

PLTORB, MOLPLT, and AIMPAC decks are written to file PUNCH at the end of the job. Thus all of these correspond to the final geometry encountered during jobs such as OPTIMIZE, SAPDOINT, IRC...

In contrast, selecting FRIEND turns the job into a CHECK run only, no matter how you set EXETYP. Thus the geometry is that encountered in \$DATA. The input is added to the PUNCH file, and may require some (usually minimal) massaging.

PLTORB and MOLPLT are written even for EXETYP=CHECK. AIMPAC requires at least RUNTYP=PROP.

The NBO program of Frank Weinhold's group can be attached to GAMESS. The input to control the natural bond order analysis is read by the add in code, so is not described here. The NBO program is available by anonymous FTP to <ftp.osc.edu>, in the directory /pub/chemistry/software/SOURCES/FORTRAN/nbo

* * * computation control switches * * *

For the most part, the default is the only sensible value, and unless you are sure

of what you are doing, these probably should not be touched.

NPRINT	=	Print/punch control flag See also EXETYP for debug info. (options -7 to 5 are primarily debug)
	=	-7 Extra printing from Boys localization.
	=	-6 debug for geometry searches
	=	-5 minimal output
	=	-4 print 2e-contribution to gradient.
	=	-3 print 1e-contribution to gradient.
	=	-2 normal printing, no punch file
	=	1 extra printing for basis,symmetry,ZMAT
	=	2 extra printing for MO guess routines
	=	3 print out property and 1e- integrals
	=	4 print out 2e- integrals
	=	5 print out SCF data for each cycle. (Fock and density matrices, current MOs same as 7, but wider 132 columns output.
	=	6
	=	7 normal printing and punching (default)
	=	8 more printout than 7. The extra output is (AO) Mulliken and overlap population analysis, eigenvalues, Lagrangians, everything in 8 plus Lowdin population analysis, final density matrix.
	=	9
NOSYM	=	0 the symmetry specified in \$DATA is used as much as possible in integrals, SCF, gradients, etc. (this is the default)
	=	1 the symmetry specified in the \$DATA group is used to build the molecule, then symmetry is not used again. Some GVB or MCSCF runs (those without a totally symmetric charge density) require you request no symmetry.
INTTYP	=	POPLE use fast Pople-Hehre routines for sp integral blocks, and HONDO Rys polynomial code for all other integrals. (default)
	=	HONDO use HONDO/Rys integrals for all integrals. This option produces very slightly more accurate integrals but is also slower.
NORMF	=	0 normalize the basis functions (default)
	=	1 no normalization
NORMP	=	0 input contraction coefficients refer to normalized Gaussian primitives. (default)
	=	1 the opposite.
ITOL	=	primitive cutoff factor (default=20)
	=	n products of primitives whose exponential factor is less than $10^{**}(-n)$ are skipped.
ICUT	=	n integrals less than $10.0^{**}(-n)$ are not saved on disk. (default = 9)

* * * restart options * * *

\$CONTRL

IREST	=	restart control options (for OPTIMIZE run restarts, see \$STATPT) Note that this option is unreliable!
	=	-1 reuse dictionary file from previous run, useful with GEOM=DAF and/or GUESS=MOSAVED. Otherwise, this option is the same as 0.
	=	0 normal run (default)
	=	1 2e restart (1-e integrals and MOs saved)
	=	2 SCF restart (1-,2-e integrals and MOs saved)
	=	3 1e gradient restart
	=	4 2e gradient restart
GEOM	=	select where to obtain molecular geometry
	=	INPUT from \$DATA input (default for IREST=0)
	=	DAF read from DICTNRY file (default otherwise)

As noted in the first chapter, binary file restart is not a well tested option!

\$SYSTEM group (optional)

This group provides global control information for your computer's operation. This is system related input, and will not seem particularly chemical to you!

TIMLIM = time limit, in minutes. Set to about 95 percent of the time limit given to the batch job so that GAMESS can stop itself gently. (default=600.0)

MWORDS = the maximum replicated memory which your job can use, on every node. This is given in units of 1,000,000 words (as opposed to 1024*1024 words), where a word is always a 64 bit quantity. Most systems allocate this memory at run time, but some more primitive systems may have an upper limit chosen at compile time. (Default=1) In case finer control over the memory is needed, this value can be given in units of words by using the keyword MEMORY instead of MWORDS.

MEMDDI = the grand total memory needed for the distributed data interface (DDI) storage, given in units of 1,000,000 words. See Chapter 5 of this manual for an extended explanation of running with MEMDDI.

note: the memory required on each node for a run using p processors is therefore MEMDDI/p + MWORDS.

The parallel runs that currently require MEMDDI are:

SCFTYP=RHF MPLEVL=2 energy or gradient
 SCFTYP=UHF MPLEVL=2 energy or gradient
 SCFTYP=ROHF MPLEVL=2 OSPT=ZAPT energy
 SCFTYP=MCSCF MPLEVL=2 energy
 SCFTYP=MCSCF FULLNR=.TRUE.
 SCFTYP=any CITYP=GUGA

All other parallel runs should enter MEMDDI=0.

PARALL = a flag to cause the distributed data parallel MP2 program to execute the parallel algorithm, even if you are running on only one node. The main purpose of this is to allow you to do EXETYP=CHECK runs to learn what the correct value of MEMDDI needs to be.

KDIAG = diagonalization control switch
 = 0 use a vectorized diagonalization routine if one is available on your machine, else use EVVRSP. (default)
 = 1 use EVVRSP diagonalization. This may be more accurate than KDIAG=0.
 = 2 use GIVEIS diagonalization (not as fast or reliable as EVVRSP)
 = 3 use JACOBI diagonalization (this is the slowest method)

COREFL = a flag to indicate whether or not GAMESS should produce a "core" file for debugging when subroutine ABRT is called to kill a job. This variable pertains only to UNIX operating systems. (default=.FALSE.)

* * * the next three refer to parallel GAMESS * * *

\$SYSTEM

The next three apply only to parallel runs, and as they are more or less obsolete, their use is discouraged.

- BALTYP = Parallel load balance scheme LOOP turns off dynamic load balancing (DLB) NXTVAL uses dynamic load balancing (default = LOOP)
- XDR = a flag to indicate whether or not messages should be converted into a generic format known as external data representation. If true, messages can exchange between machines of different vendors, at the cost of performing the data type conversions. (default=.FALSE.) --inactive at present--

On machines which do not use TCGMSG (the IBM SP, the Intel Paragon, the CM-5), the BALTYP and XDR variables are ignored. LOOP balancing is used exclusively, and there is no possible transfer of data to another vendor so XDR is irrelevant.

- PTIME = a logical flag to print extra timing info during parallel runs. This is not currently implemented.

\$BASIS group (optional)

This group allows certain standard basis sets to be easily given. If this group is omitted, the basis set must be given instead in the \$DATA group.

GBASIS	=	Name of the Gaussian basis set.
	=	MINI Huzinaga's 3 gaussian minimal basis set. Available H-Rn.
	=	MIDI Huzinaga's 21 split valence basis set. Available H-Rn.
	=	STO Pople's STO-NG minimal basis set. Available H-Xe, for NGAUSS=2,3,4,5,6.
	=	N21 Pople's N-21G split valence basis set. Available H-Xe, for NGAUSS=3. Available H-Ar, for NGAUSS=6.
	=	N31 Pople's N-31G split valence basis set. Available H-Ne,P-Cl for NGAUSS=4. Available H-He,C-F for NGAUSS=5. Available H-Ar, for NGAUSS=6. For Ga-Kr, N31 selects the BC basis.
	=	N311 Pople's "triple split" N-311G basis set. Available H-Ne, for NGAUSS=6. Selecting N311 implies MC for Na-Ar.
	=	DZV "double zeta valence" basis set. a synonym for DH for H,Li,Be-Ne,Al-Cl. (14s,9p,3d)/[5s,3p,1d] for K-Ca. (14s,11p,5d)/[6s,4p,1d] for Ga-Kr.
	=	DH Dunning/Hay "double zeta" basis set. (3s)/[2s] for H. (9s,4p)/[3s,2p] for Li. (9s,5p)/[3s,2p] for Be-Ne. (11s,7p)/[6s,4p] for Al-Cl.
	=	TZV "triple zeta valence" basis set. (5s)/[3s] for H. (10s,3p)/[4s,3p] for Li. (10s,6p)/[5s,3p] for Be-Ne. a synonym for MC for Na-Ar. (14s,9p)/[8s,4p] for K-Ca. (14s,11p,6d)/[10s,8p,3d] for Sc-Zn.
	=	MC McLean/Chandler "triple split" basis. (12s,9p)/[6s,5p] for Na-Ar. Selecting MC implies 6-311G for H-Ne.

* * * the next two are ECP bases only * * *

GBASIS	=	SBKJC Stevens/Basch/Krauss/Jasien/Cundari valence basis set, for Li-Rn. This choice implies an unscaled -31G basis for H-He.
	=	HW Hay/Wadt valence basis. This is a -21 split, available Na- Xe, except for the transition metals. This implies a 3-21G basis for H-Ne.

* * * semiempirical basis sets * * *

The elements for which these exist can be found in the 'further information' section of this manual. If you pick one of these, all other data in this group is ignored. Semi-empirical runs actually use valence-only STO bases, not GTOs.

- GBASIS = MNDO selects MNDO model hamiltonian
 = AM1 selects AM1 model hamiltonian
 = PM3 selects PM3 model hamiltonian
- NGAUSS = the number of Gaussians (N). This parameter pertains only to GBASIS=STO, N21, N31, or N311.
- NDFUNC = number of heavy atom polarization functions to be used. These are usually d functions, except for MINI/MIDI. The term "heavy" means Na on up when GBASIS=STO, HW, or N21, and from Li on up otherwise. The value may not exceed 3. The variable POLAR selects the actual exponents to be used, see also SPLIT2 and SPLIT3. (default=0)
- NFFUNC = number of heavy atom f type polarization functions to be used on Li-Cl. This may only be input as 0 or 1. (default=0)
- NPFUNC = number of light atom, p type polarization functions to be used on H-He. This may not exceed 3, see also POLAR. (default=0)
- DIFFSP = flag to add diffuse sp (L) shell to heavy atoms. Heavy means Li-F, Na-Cl, Ga-Br, In-I, Tl-At. The default is .FALSE.
- DIFFS = flag to add diffuse s shell to hydrogens. The default is .FALSE.

Warning: if you use diffuse functions, please read QMTTOL and INTTYP in the \$CONTRL group for numerical concerns.

- POLAR = exponent of polarization functions
 = POPLE (default for all other cases)
 = POPN311 (default for GBASIS=N311, MC)
 = DUNNING (default for GBASIS=DH, DZV)
 = HUZINAGA (default for GBASIS=MINI, MIDI)
 = HONDO7 (default for GBASIS=TZV)
- SPLIT2 = an array of splitting factors used when NDFUNC or NPFUNC is 2.
 Default=2.0,0.5
- SPLIT3 = an array of splitting factors used when NDFUNC or NPFUNC is 3.
 Default=4.00,1.00,0.25
- EXTFIL = a flag to read basis sets from an external file, defined by EXTBAS, instead of \$DATA. No external file is provided with GAMESS, instead you would supply your own. The GBASIS keyword must give an 8 character string, obviously not using any internally stored names. Every atom must be defined in the external file by a line giving the chemical symbol, and this string. Following this header line, give the basis in free format \$DATA

style, containing only S, P, D, F, G, and L shells, and terminating each atom by the usual blank line. The GBASIS string allows you to have several families of bases in the same file, identified by different strings. (default=.false.)

The splitting factors are from the Pople school, and are probably too far apart. See for example the Binning and Curtiss paper. For example, the SPLIT2 value will usually cause an INCREASE over the 1d energy at the HF level for hydrocarbons.

The actual exponents used for polarization functions, as well as for diffuse sp or s shells, are described in the 'Further References' section of this manual. This section also describes the sp part of the basis set chosen by GBASIS fully, with all references cited.

Note that GAMESS always punches a full \$DATA group. Thus, if \$BASIS does not quite cover the basis you want, you can obtain this full \$DATA group from EXETYP=CHECK, and then change polarization exponents, add Rydbergs, etc.

\$DATA/\$DATAS/\$DATAL

\$DATA group (required)

\$DATAS group (if NESC chosen, gives small component basis)

\$DATAL group (if NESC chosen, gives large component basis)

This group describes the global molecular data such as point group symmetry, nuclear coordinates, and possibly the basis set. It consists of a series of free format card images. See \$RELWFN for more information on large and small component basis sets. The input structure of \$DATAS and \$DATAL is identical to the COORD=UNIQUE \$DATA input.

-1- TITLE a single descriptive title card.

-2- GROUP, NAXIS

GROUP is the Schoenflies symbol of the symmetry group, you may choose from C1, Cs, Ci, Cn, S2n, Cnh, Cnv, Dn, Dnh, Dnd, T, Th, Td, O, Oh.

NAXIS is the order of the highest rotation axis, and must be given when the name of the group contains an N. For example, "Cnv 2" is C2v. "S2n 3" means S6. Use of NAXIS up to 8 is supported in each axial groups.

For linear molecules, choose either Cnv or Dnh, and enter NAXIS as 4. Enter atoms as Dnh with NAXIS=2. If the electronic state of either is degenerate, check the note about the effect of symmetry in the electronic state in the SCF section of REFS.DOC.

In order to use GAMESS effectively, you must be able to recognize the point group name for your molecule. This presupposes a knowledge of group theory at about the level of Cotton's "Group Theory", Chapter 3.

Armed with only the name of the group, GAMESS is able to exploit the molecular symmetry throughout almost all of the program, and thus save a great deal of computer time. GAMESS does not require that you know very much else about group theory, although a deeper knowledge (character tables, irreducible representations, term symbols, and so on) is useful when dealing with the more sophisticated wavefunctions.

Cards -3- and -4- are quite complicated, and are rarely given. A *SINGLE* blank card may replace both cards -3- and -4-, to select the 'master frame', which is defined on the next page. If you choose to enter a blank card, skip to the bottom of the next page.

Note ! If the point group is C₁ (no symmetry), skip over cards -3- and -4- (which means no blank card).

-3- X1, Y1, Z1, X2, Y2, Z2

For C1 group, there is no card -3- or -4-.

For Ci group, give one point, the center of inversion.

For Cs group, any two points in the symmetry plane.

For axial groups, any two points on the principal axis.

For tetrahedral groups, any two points on a two-fold axis.

For octahedral groups, any two points on a four-fold axis.

-4- X3, Y3, Z3, DIRECT

third point, and a directional parameter.

For CS group, one point of the symmetry plane, noncollinear with points 1 and 2.

For CI group, there is no card -4-.

For other groups, a generator sigma-v plane (if any) is the (x,z) plane of the local frame (CNV point groups).

A generator sigma-h plane (if any) is the (x,y) plane of the local frame (CNH and dihedral groups).

A generator C2 axis (if any) is the x-axis of the local frame (dihedral groups).

The perpendicular to the principal axis passing through the third point defines a direction called D1. If DIRECT='PARALLEL', the x-axis of the local frame coincides with the direction D1. If DIRECT='NORMAL', the x-axis of the local frame is the common perpendicular to D1 and the principal axis, passing through the intersection point of these two lines. Thus D1 coincides in this case with the negative y axis.

The 'master frame' is just a standard orientation for the molecule. By default, the 'master frame' assumes that

1. z is the principal rotation axis (if any),
2. x is a perpendicular two-fold axis (if any),
3. xz is the sigma-v plane (if any), and
4. xy is the sigma-h plane (if any).

Use the lowest number rule that applies to your molecule.

Some examples of these rules:

Ammonia (C3v): the unique H lies in the XZ plane (R1,R3).

Ethane (D3d): the unique H lies in the YZ plane (R1,R2).

Methane (Td): the H lies in the XYZ direction (R2). Since there is more than one 3-fold, R1 does not apply.

HP=O (Cs): the mirror plane is the XY plane (R4).

In general, it is a poor idea to try to reorient the molecule. Certain sections of the program, such as the orbital symmetry assignment, do not know how to deal with cases where the 'master frame' has been changed.

Linear molecules (C4v or D4h) must lie along the z axis, so do not try to reorient linear molecules.

You can use EXETYP=CHECK to quickly find what atoms are generated, and in what order. This is typically necessary in order to use the general \$ZMAT coordinates.

Depending on your choice for COORD in \$CONTROL,

if COORD=UNIQUE, follow card sequence U

if COORD=HINT, follow card sequence U

if COORD=CART, follow card sequence C

if COORD=ZMT, follow card sequence G

if COORD=ZMTMPC, follow card sequence M

\$DATA/\$DATAS/\$DATAL

Card sequence U is the only one which allows you to define a completely general basis here in \$DATA.

Recall that UNIT in \$CONTRL determines the distance units.

-5U- Atom input. Only the symmetry unique atoms are input, GAMESS will generate the symmetry equivalent atoms according to the point group selected above.

if COORD=UNIQUE NAME, ZNUC, X, Y, Z

NAME = 10 character atomic name, used only for printout. Thus you can enter H or Hydrogen, or whatever.
 ZNUC = nuclear charge. It is the nuclear charge which actually defines the atom's identity.
 X,Y,Z = Cartesian coordinates.

if COORD=HINT

NAME,ZNUC,CONX,R,ALPHA,BETA,SIGN,POINT1,POINT2,POINT3

NAME = 10 character atomic name (used only for print out).

ZNUC = nuclear charge.

CONX = connection type, choose from

'LC'	linear conn.	'CCPA' central conn.
'PCC'	planar central conn.	with polar atom
'NPCC'	non-planar central conn.	'TCT' terminal conn.
'PTC'	planar terminal conn.	with torsion

R = connection distance.

ALPHA= first connection angle

BETA = second connection angle

SIGN = connection sign, '+' or '-'

POINT1, POINT2, POINT3 =

connection points, a serial number of a previously input atom, or one of 4 standard points: O,I,J,K (origin and unit points on axes of master frame).
 defaults: POINT1='O', POINT2='I', POINT3='J'

ref- R.L. Hilderbrandt, J.Chem.Phys. 51, 1654 (1969).

You cannot understand HINT input without reading this.

Note that if ZNUC is negative, the internally stored basis for ABS(ZNUC) is placed on this center, but the calculation uses ZNUC=0 after this. This is useful for basis set superposition error (BSSE) calculations.

* * * If you gave \$BASIS, continue entering cards -5U- until all the unique atoms have been specified. When you are done, enter a " \$END " card.
 * * * If you did not, enter cards -6U-, -7U-, -8U-.

-6U- GBASIS, NGAUSS, (SCALF(i),i=1,4)

GBASIS has exactly the same meaning as in \$BASIS. You may choose from MINI, MIDI, STO, N21, N31, N311, DZV, DH, BC, TZV, MC, SBKJC, or HW. In addition, you may choose S, P, D, F, G, or L to enter an explicit basis set. Here, L means an s and p shell with a common exponent.

In addition, GBASIS may be defined as MCP, to indicate that the current atom is represented by a model core potential. MCP must be followed by the keyword READ to indicate that the basis functions are read using the sequence -6U-, -7U-, and -8U-, as presently there are no built in basis sets. In addition, MCP implies that the parameters of the model core potentials together with core basis functions are in the input stream in a \$MCP group.

NGAUSS is the number of Gaussians (N) in the Pople style basis, or user input general basis. It has meaning only for GBASIS=STO, N21, N31, or N311, and S,P,D,F,G, or L.

Up to four scale factors may be entered. If omitted, standard values are used. They are not documented as every GBASIS treats these differently. Read the source code if you need to know more. They are seldom given.

* * * If GBASIS is not S,P,D,F,G, or L, either add more shells by repeating card -6U-, or go on to -8U-.

* * * If GBASIS=S,P,D,F,G, or L, enter NGAUSS cards -7U-.

-7U- IG, ZETA, C1, C2

IG = a counter, IG takes values 1, 2, ..., NGAUSS.

ZETA = Gaussian exponent of the IG'th primitive.

C1 = Contraction coefficient for S,P,D,F,G shells, and for the s function of L shells.

C2 = Contraction coefficient for the p in L shells.

* * * For more shells on this atom, go back to card -6U-.

* * * If there are no more shells, go on to card -8U-.

-8U- A blank card ends the basis set for this atom.

Continue entering atoms with -5U- through -8U- until all are given, then terminate the group with a " \$END " card.

- - - this is the end of card sequence U - - -

COORD=CART input:

-5C- Atom input.

Cartesian coordinates for all atoms must be entered. They may be arbitrarily rotated or translated, but must possess the actual point group symmetry. GAMESS will reorient the molecule into the 'master frame', and determine which atoms are the unique ones. Thus, the final order of the atoms may be different from what you enter here.

NAME, ZNUC, X, Y, Z

NAME = 10 character atomic name, used only for printout. Thus you can enter H or Hydrogen, or whatever.

ZNUC = nuclear charge. It is the nuclear charge which actually defines the atom's identity.

X,Y,Z = Cartesian coordinates.

Continue entering atoms with card -5C- until all are given, and then terminate the group with a " \$END " card.

- - - this is the end of card sequence C - - -

COORD=ZMT input: (GAUSSIAN style internals)

- 5 G- ATOM

Only the name of the first atom is required.
See -8G- for a description of this information.

- 6 G- ATOM i1 BLENGTH

Only a name and a bond distance is required for atom 2.
See -8G- for a description of this information.

- 7 G- ATOM i1 BLENGTH i2 ALPHA

Only a name, distance, and angle are required for atom 3.
See -8G- for a description of this information.

- 8 G- ATOM i1 BLENGTH i2 ALPHA i3 BETA i4

ATOM is the chemical symbol of this atom. It can be followed by numbers, if desired, for example Si3. The chemical symbol implies the nuclear charge.
i1 defines the connectivity of the following bond.
BLENGTH is the bond length "this atom-atom i1".
i2 defines the connectivity of the following angle.
ALPHA is the angle "this atom-atom i1-atom i2".
i3 defines the connectivity of the following angle.
BETA is either the dihedral angle "this atom-atom i1- atom i2-atom i3", or perhaps a second bond angle "this atom-atom i1-atom i3".

i4 defines the nature of BETA, If BETA is a dihedral angle, i4=0 (default). If BETA is a second bond angle, i4=+/-1. (sign specifies one of two possible directions).

- Repeat -8G- for atoms 4, 5, ...
 - The use of ghost atoms is possible, by using X or BQ for the chemical symbol. Ghost atoms preclude the option of an automatic generation of \$ZMAT.
 - The connectivity i1, i2, i3 may be given as integers, 1, 2, 3, 4, 5,... or as strings which match one of the ATOMS. In this case, numbers must be added to the ATOM strings to ensure uniqueness!
 - In -6G- to -8G-, symbolic strings may be given in place of numeric values for BLENGTH, ALPHA, and BETA. The same string may be repeated, which is handy in enforcing symmetry. If the string is preceded by a minus sign, the numeric value which will be used is the opposite, of course. Any mixture of numeric data and symbols may be given. If any strings were given in -6G- to -8G-, you must provide cards -9G- and -10G-, otherwise you may terminate the group now with a " \$END " card.
-

-9G- A blank line terminates the Z-matrix section.

-10G- STRING VALUE

STRING is a symbolic string used in the Z-matrix.

VALUE is the numeric value to substitute for that string.

Continue entering -10G- until all STRINGS are defined. Note that any blank card encountered while reading -10G- will be ignored. GAMESS regards all STRINGS as variables (constraints are sometimes applied in \$STATPT). It is not necessary to place constraints to preserve point group symmetry, as GAMESS will never lower the symmetry from that given at -2-. When you have given all STRINGS a VALUE, terminate the group with a " \$END " card.

- - - this is the end of card sequence G - - -

The documentation for sequence G above and sequence M below presumes you are reasonably familiar with the input to GAUSSIAN or MOPAC. It is probably too terse to be understood very well if you are unfamiliar with these. A good tutorial on both styles of Z-matrix input can be found in Tim Clark's book "A Handbook of Computational Chemistry", published by John Wiley & Sons, 1985.

Both Z-matrix input styles must generate a molecule which possesses the symmetry you requested at -2-. If not, your job will be terminated automatically.

COORD=ZMTMPC input: (MOPAC style internals)

- 5 M - ATOM

\$DATA/\$DATAS/\$DATAI

Only the name of the first atom is required.
See -8M- for a description of this information.

- 6 M - ATOM BLENGTH

Only a name and a bond distance is required for atom 2.
See -8M- for a description of this information.

- 7 M - ATOM BLENGTH j1 ALPHA j2

Only a bond distance from atom 2, and an angle with respect to atom 1 is required for atom 3. If you prefer to hook atom 3 to atom 1, you must give connectivity as in -8M-.
See -8M- for a description of this information.

- 8 M - ATOM BLENGTH j1 ALPHA j2 BETA j3 i1 i2 i3

ATOM, BLENGTH, ALPHA, BETA, i1, i2 and i3 are as described at -8G-. However, BLENGTH, ALPHA, and BETA must be given as numerical values only. In addition, BETA is always a dihedral angle. i1, i2, i3 must be integers only.

The j1, j2 and j3 integers, used in MOPAC to signal optimization of parameters, must be supplied but are ignored here. You may give them as 0, for example.

Continue entering atoms 3, 4, 5, ... with -8M- cards until all are given, and then terminate the group by giving a " \$END " card.

- - - this is the end of card sequence M - - -

This is the end of \$DATA!

If you have any doubt about what molecule and basis set you are defining, or what order the atoms will be generated in, simply execute an EXETYP=CHECK job to find out!

\$ZMAT group (required if NZVAR is nonzero in \$CONTRL)

This group lets you define the internal coordinates in which the gradient geometry search is carried out. These need not be the same as the internal coordinates used in \$DATA. The coordinates may be simple Z-matrix types, delocalized coordinates, or natural internal coordinates.

You must input a total of $M=3N-6$ internal coordinates ($M=3N-5$ for linear molecules). NZVAR in \$CONTRL can be less than M IF AND ONLY IF you are using linear bends. It is also possible to input more than M coordinates if they are used to form exactly M linear combinations for new internals. These may be symmetry coordinates or natural internal coordinates. If $NZVAR > M$, you must input IJS and SIJ below to form M new coordinates. See DECOMP in \$FORCE for the only circumstance in which you may enter a larger NZVAR without giving SIJ and IJS.

**** IZMAT defines simple internal coordinates ****

IZMAT is an array of integers defining each coordinate.

The general form for each internal coordinate is code number,I,J,K,L,M,N

IZMAT

- =1 followed by two atom numbers. (I-J bond length)
- =2 followed by three numbers. (I-J-K bond angle)
- =3 followed by four numbers. (dihedral angle) Torsion angle between planes I-J-K and J-K-L.
- =4 followed by four atom numbers. (atom-plane) Out-of-plane angle from bond I-J to plane J-K-L.
- =5 followed by three numbers. (I-J-K linear bend) Counts as 2 coordinates for the degenerate bend, normally J is the center atom. See \$LIBE.
- =6 followed by five atom numbers. (dihedral angle) Dihedral angle between planes I-J-K and K-L-M.
- =7 followed by six atom numbers. (ghost torsion) Let A be the midpoint between atoms I and J, and B be the midpoint between atoms M and N. This coordinate is the dihedral angle A-K-L-B. The atoms I,J and/or M,N may be the same atom number. (If $I=J$ AND $M=N$, this is a conventional torsion). Examples: N_2H_4 , or, with one common pair, H_2POH .

Example - a nonlinear triatomic, atom 2 in the middle:

```
$ZMAT IZMAT(1)=1,1,2, 2,1,2,3, 1,2,3 $END
```

This sets up two bonds and the angle between them. The blanks between each coordinate definition are not necessary, but improve readability mightily.

**** the next define delocalized coordinates ****

DLC is a flag to request delocalized coordinates. (default is .FALSE.)

AUTO is a flag to generate all redundant coordinates, automatically. The DLC space will consist of all non-redundant combinations of these which can be found. The list of redundant coordinates will consist of bonds, angles, and torsions only. (default is .FALSE.)

NONVDW is an array of atom pairs which are to be joined by a bond, but might be skipped by the routine that automatically includes all distances shorter than

the sum of van der Waals radii. Any angles and torsions associated with the new bond(s) are also automatically included.

The format for IXZMAT, IRZMAT, IFZMAT is that of IZMAT:

IXZMAT is an extra array of simple internal coordinates which you want to have added to the list generated by AUTO. Unlike NONVDW, IXZMAT will add only the coordinate(s) you specify.

IRZMAT is an array of simple internal coordinates which you would like to remove from the AUTO list of redundant coordinates. It is sometimes necessary to remove a torsion if other torsions around a bond are being frozen, to obtain a nonsingular G matrix.

IFZMAT is an array of simple internal coordinates which you would like to freeze. See also FVALUE below. Note that IFZMAT/FVALUE work only with DLC, see the IFREEZ option in \$STATPT to freeze coordinates if you wish to freeze simple or natural coordinates.

FVALUE is an array of values to which the internal coordinates should be constrained. It is not necessary to input \$DATA such that the initial values match these desired final values, but it is helpful if the initial values are not too far away.

**** SIJ,IJS define natural internal coordinates ****

SIJ is a transformation matrix of dimension NZVAR x M, used to transform the NZVAR internal coordinates in IZMAT into M new internal coordinates. SIJ is a sparse matrix, so only the non-zero elements are given, by using the IJS array described below. The columns of SIJ will be normalized by GAMESS. (Default: SIJ = I, unit matrix)

IJS is an array of pairs of indices, giving the row and column index of the entries in SIJ.

example - if the above triatomic is water, using

IJS(1) = 1,1, 3,1, 1,2, 3,2, 2,3

SIJ(1) = 1.0, 1.0, 1.0,-1.0, 1.0

gives the matrix S=

1.0	1.0	0.0
0.0	0.0	1.0
1.0	-1.0	0.0

which defines the symmetric stretch, asymmetric stretch, and bend of water.

references for natural internal coordinates:

P.Pulay, G.Fogarasi, F.Pang, J.E.Boggs J.Am.Chem.Soc. 101, 2550-2560(1979)

G.Fogarasi, X.Zhou, P.W.Taylor, P.Pulay J.Am.Chem.Soc. 114, 8191-8201(1992)

reference for delocalized coordinates:

J.Baker, A. Kessi, B.Delley J.Chem.Phys. 105, 192-212(1996)

\$LIBE group (required if linear bends are used in \$ZMAT)

A degenerate linear bend occurs in two orthogonal planes, which are specified with the help of a point A. The first bend occurs in a plane containing the atoms I,J,K and the user input point A. The second bend is in the plane perpendicular to this, and containing I,J,K. One such point must be given for each pair of bends used.

APTS(1)= x1,y1,z1,x2,y2,z2,... for linear bends 1,2,...

Note that each linear bend serves as two coordinates, so that if you enter 2 linear bends (HCCH, for example), the correct value of NZVAR is M-2, where M=3N-6 or 3N-5, as appropriate.

\$SCF

\$SCF group relevant if SCFTYP = RHF, UHF, or ROHF,
 required if SCFTYP = GVB)

This group of parameters provides additional control over the RHF, UHF, ROHF, or GVB SCF steps. It must be given for GVB open shell or perfect pairing wavefunctions.

DIRSCF = a flag to activate a direct SCF calculation, which is implemented for all the Hartree-Fock type wavefunctions: RHF, ROHF, UHF, and GVB. This keyword also selects direct MP2 computation. The default of .FALSE. stores integrals on disk storage for a conventional SCF calculation.

FDIFF = a flag to compute only the change in the Fock matrices since the previous iteration, rather than recomputing all two electron contributions. This saves much CPU time in the later iterations. This pertains only to direct SCF, and has a default of .TRUE. This option is implemented only for the RHF, ROHF, UHF cases.
 Cases with many diffuse functions in the basis set sometimes oscillate at the end, rather than converging. Turning this parameter off will normally give convergence.

- The next flags affect convergence rates.

NOCONV = .TRUE. means neither SOSCF nor DIIS will be used.
 The default is .FALSE., making the choice of the primary converger as follows:

 for RHF, GVB, or Abelian group ROHF, use SOSCF.

 for any DFT, UHF, or non-Abelian ROHF, use DIIS.

DIIS = selects Pulay's DIIS interpolation.

SOSCF = selects second order SCF orbital optimization.

Once either DIIS or SOSCF are initiated, the following less important accelerators are put in abeyance:

EXTRAP = selects Pople extrapolation of the Fock matrix.

DAMP = selects Davidson damping of the Fock matrix.

SHIFT = selects level shifting of the Fock matrix.

RSTRCT = selects restriction of orbital interchanges.

DEM = selects direct energy minimization, which is implemented only for RHF.
 (default=.FALSE.)

defaults for	EXTRAP	DAMP	SHIFT	RSTRCT	DIIS	SOSCF
ab initio:	T	F	F	F	F/T	T/F
semiempirical:	T	F	F	F	F	F

The above parameters are implemented for all SCF wavefunction types, except that DIIS will work for GVB only for those cases with NPAIR=0 or NPAIR=1.

- These parameters fine tune the various convergers.

CONV = SCF density convergence criteria. Convergence is reached when the density change between two consecutive SCF cycles is less than this in absolute value. One more cycle will be executed after reaching

convergence. Less accuracy in CONV gives questionable gradients. The default is 1.0d-05, except runs involving CI or MP2 gradients or CC energies use 1.0d-06.

- SOGTOL = second order gradient tolerance. SOSCF will be initiated when the orbital gradient falls below this threshold. (default=0.25 au)
- ETHRSH = energy error threshold for initiating DIIS. The DIIS error is the largest element of $e=FDS-SDF$. Increasing ETHRSH forces DIIS on sooner. (default = 0.5 Hartree)
- MAXDII = Maximum size of the DIIS linear equations, so that at most MAXDII-1 Fock matrices are used in the interpolation. (default=10)
- DEMCUT = Direct energy minimization will not be done once the density matrix change falls below this threshold. (Default=0.5)
- DMPCUT = Damping factor lower bound cutoff. The damping factor will not be allowed to drop below this value. (default=0.0)
- note : The damping factor need not be zero to achieve valid convergence (see Hsu, Davidson, and Pitzer, J.Chem.Phys., 65, 609 (1976), see especially the section on convergence control), but it should not be astronomical either.

For more info on the convergence methods, see the 'Further Information' section.

- Miscellaneous options.

- NPUNCH = SCF punch option
 = 0 do not punch out the final orbitals
 = 1 punch out the occupied orbitals
 = 2 punch out occupied and virtual orbitals The default is NPUNCH = 2.
- UHFNOS = flag controlling generation of the natural orbitals of a UHF function. (default=.FALSE.)
- MVOQ = 0 Skip MVO generation (default)
 = n Form modified virtual orbitals, using a cation with n electrons removed. Implemented for RHF, ROHF, and GVB. If necessary to reach a closed shell cation, the program might remove n+1 electrons. Typically, n will be about 6.
 = -1 The cation used will have each valence orbital half filled, to produce MVOs with valence-like character in all regions of the molecule. Implemented for RHF and ROHF only.
- ACAVO = Flag to request Approximate Correlation-Adapted Virtual Orbitals. Implemented for RHF, ROHF, and GVB. The default is .FALSE.
- PACAVO = Parameters used to define the ACAVO generating operator, which is the operator $a^*T + b^*V_{ne} + c^*J_{core} + d^*J_{val} + e^*K_{core} + f^*K_{val}$

The default corresponds to Whitten orbitals, J.L.Whitten, J.Chem.Phys. 56, 458-546(1972) which maximize the exchange interaction with the valence orbitals, PACOVO(1)=0,0,0,0,0,-1.0. A better set of parameters, in terms of possibly producing a lower CI-SD energy, is PACAVO(1)= 0.02,0.02,0.0,0.10,0.0,-1.0

- options for virial scaling

VTSCAL = A flag to request that the virial theorem be satisfied. An analysis of the total energy as an exact sum of orbital kinetic energies is printed. The default is .FALSE.

This option is implemented for RHF, UHF, and ROHF, for RUNTYP=ENERGY, OPTIMIZE, or SADPOINT. Related input is as follows:

SCALF = initial exponent scale factor when VTSCAL is in use, useful when restarting. The default is 1.0.

MAXVT = maximum number of iterations (at a single geometry) to satisfy the energy virial theorem. The default is 20.

VTCONV = convergence criterion for the VT, which is satisfied when $2\langle T \rangle + \langle V \rangle + R \times dE/dR$ is less than VTCONV. The default is 1.0D-6 Hartree.

For more information on this option, which is most economically employed during a geometry search, see

M.Lehd and F.Jensen, J.Comput.Chem. 12, 1089-1096(1991).

- GVB/ROHF options

The next parameters define the GVB wavefunction. Note that ALPHA and BETA also have meaning for ROHF. See also MULT in the \$CONTRL group. The GVB wavefunction assumes orbitals are in the order core, open, pairs.

NCO = The number of closed shell orbitals. The default almost certainly should be changed! (default=0).

NSETO = The number of sets of open shells in the function. Maximum of 10. (default=0)

NO = An array giving the degeneracy of each open shell set. Give NSETO values. (default=0,0,0,...).

NPAIR = The number of geminal pairs in the -GVB- function. Maximum of 12. The default corresponds to open shell SCF (default=0).

CICOEF = An array of ordered pairs of CI coefficients for the -GVB- pairs. For example, a two pair case for water, say, might be CICOEF(1)=0.95,-0.05,0.95,-0.05. If not normalized, as in the default, they will be. This parameter is useful in restarting a GVB run, with the current CI

coefficients. (default = 0.90,-0.20,0.90,-0.20,...)

COUPLE = A switch controlling the input of F, ALPHA, and BETA. The default is to use internally stored values for these variables. Note ALPHA and BETA can be given for -ROHF-, as well as -GVB-. (Default=.FALSE.)

F = An vector of fractional occupations.

ALPHA = An array of A coupling coefficients given in lower triangular order.

BETA = An array of B coupling coefficients given in lower triangular order.

Note : The default for F, ALPHA, and BETA depends on the state chosen. Defaults for the most commonly occurring cases are internally stored.

For more discussion of GVB/ROHF input see the 'further information' section

\$SCFMI group (optional, relevant if SCFTYP=RHF)

The SCF-MI method is a modification of the Roothaan equations that avoids basis set superposition error (BSSE) in intermolecular interaction calculations, by expanding each monomer's orbitals using only its own basis set. Thus, the resulting orbitals are not orthogonal. The presence of a \$SCFMI group in the input triggers the use of this option.

The implementation is limited to two monomers, treated at the RHF level. The energy, gradient, and therefore numerical hessian are available. The SCF step may be run in direct SCF mode. The first 4 parameters must be given. All atoms of monomer A must be given in \$DATA before the atoms of monomer B.

NA	=	number of doubly occupied MOs on fragment A.
NB	=	number of doubly occupied MOs on fragment B.
MA	=	number of basis functions on fragment A.
MB	=	number of basis functions on fragment B.
ITER	=	maximum number of SCF-MI cycles, overriding the usual MAXIT value. (default is 50).
DTOL	=	SCF-MI density convergence criteria. (default is 1.0d-10)
ALPHA	=	possible level shift parameter. (default is 0.0, meaning shifting is not used)
IOPT	=	prints additional debug information. = 0 standard output (default) = 1 print for each SCF-MI cycle MOs, overlap between the MOs, CPU times. = 2 print some extra informations in secular systems solution.
MSHIFT	=	debugging option that permits to shift all the memory pointer of the SCF-MI section of code of the quantity MSHIFT (default is 0).

"Modification of Roothaan Equations to Exclude BSSE from Molecular Interaction Calculations"
E. Gianinetti, M. Raimondi, E. Tornaghi Int. J. Quantum Chem. 60, 157 (1996)

A. Famulari, E. Gianinetti, M. Raimondi, and M. Sironi Int. J. Quantum Chem. (1997),
submitted.

\$DFT group (relevant if SCFTYP=RHF,UHF,ROHF)

Note that if DFTTYP=NONE, an ab initio calculation will be performed, rather than density functional theory.

This group permits the use of various one electron (usually empirical) operators instead of the true many electron Hamiltonian. Two programs are provided, METHOD= GRID or GRIDFREE. The programs have different functionals available, and so the keyword DFTTYP and other associated inputs are documented separately below. Every functional that has the same name in both lists is the identical functional, but each METHOD has a few functionals that are missing in the other.

The grid free implementation is based on the use of resolution of the identity to simplify integrals so that they may be analytically evaluated, without using grid quadratures. The grid free DFT computations in their present form have various numerical errors, primarily in the gradient vectors. Please do not use the grid-free DFT program without reading the discussion in the 'Further References' section regarding the gradient accuracy.

The grid based DFT uses a typical grid quadrature to compute integrals over the rather complicated functionals.

Achieving a self-consistent field with DFT is somewhat more difficult than for normal HF, so DIIS is the default converger. Since the DFT iterations are also more time consuming, the use of GUESS=MOREAD may be very helpful.

Both DFT programs will run in parallel.

DFTTYP = NONE means no DFT is performed (default)

METHOD = selects grid based DFT or grid free DFT.
 = GRID Grid based DFT (default)
 = GRIDFREE Grid free DFT

----- options for METHOD=GRID -----

DFTTYP = specifies exchange and correlation functionals.
 pure exchange functionals (no correlation):
 = SLATER Slater exchange
 = BECKE Becke 1988 exchange
 = GILL Gill 1996 exchange
 = PBE Perdew-Burke-Ernzerhof (PBE) exchange
 Note that the PBE correlation functional is not implemented.
 pure correlation functionals (HF exchange):
 = WN Vosko-Wilk-Nusair correlation, using their electron gas formula 5 (VWN5)
 = LYP Lee-Yang-Parr correlation
 = OP One-parameter Progressive correlation combination functionals:
 = SVWN SLATER exchange + VWN5 correlation
 Called LDA/LSDA by physicists for RHF/UHF.
 = SLYP SLATER exchange + LYP correlation

= SOP	SLATER exchange + OP correlation
= BVWN	BECKE exchange + VWN5 correlation
= BLYP	BECKE exchange + LYP correlation
= BOP	BECKE exchange + OP correlation
= GVWN	GILL exchange + VWN5 correlation
= GLYP	GILL exchange + LYP correlation
= GOP	GILL exchange + OP correlation
= PBEVWN	PBE exchange + VWN5 correlation
= PBELYP	PBE exchange + LYP correlation
= PBEOP	PBE exchange + OP correlation
hybrid functionals:	
= BHHLYP	HF and BECKE exchange + LYP correlation
= B3LYP	this is a hybrid method combining five functionals, namely Becke + Slater + HF exchange and LYP + VWN5 correlation.

An extensive bibliography for these functionals can be found in the 'Further References' section of this manual.

NRAD	=	number of radial grids in Euler-Maclaurin quadrature. (default=96)
NTHE	=	number of angle theta grids in Gauss-Legendre quadrature. (default=12)
NPHI	=	number of angle phi grids in Gauss-Legendre quadrature. NPHI should be double NTHE so that points are spherically distributed. (default=24)

NRAD*NTHE*NPHI grid points will be constructed around each atom. Time is linear in the number of grid points, so be careful. Energies can be compared only when the identical grid density has been used, analogous to needing to compare with the identical basis set expansions. A very accurate "army grade" grid capable of producing an integration error less than a microHartree/atom is NRAD=96 NTHE=36 NPHI=72.

The default grid has an error probably no worse than about 20 microHartree/atom, depending on the type of atom.

NRADO, NTHEO, NPHIO define a smaller grid used during the SCF iterations before some initial convergence is reached. After that, the full grid defined by NRAD, NTHE, NPHI will be used. This can save considerable CPU time in the early SCF iterations.

SWITCH	=	when the change in the density matrix between iterations falls below this threshold, switch to use of the desired full grid (default=3.0E-4)
NRADO	=	same as NRAD, but defines initial (smaller) grid.
NTHEO	=	same as NTHE, but defines initial (smaller) grid.
NPHIO	=	same as NPHI, but defines initial (smaller) grid.

Default values for the initial grid depend upon NRAD, NTHE, and NPHI. For the default

full grid settings, the initial grid is NRADO=24, NTHEO=8, NPHIO=16, for other values the formula is NRADO the larger of NRAD/4 or 24, for NTHEO the larger of NTHE/3 or 8, and for NPHIO the larger of NPHI/3 or 16. In case of slow convergence of the SCF or if using the "army grade grid", NRADO=48 NTHEO=12 NPHIO=24 and SWITCH=1.0E-4 may be better. Numerical hessian runs set the coarse grid to the same size as the full grid, by default.

THRESH = threshold for ignoring small contributions to the Fock matrix. The default is designed to produce no significant energy loss, even when the grid is as good as "army grade". If for some reason you want to turn all threshold tests off, of course requiring more CPU, enter 1.0e-15.
default: 1.0e-4/Natoms/NRAD/NTHE/NPHI

----- options for METHOD=GRIDFREE -----

DFTTYP	= NONE	means ab initio computation (default) exchange functionals:
	= XALPHA	X-Alpha exchange (alpha=0.7)
	= SLATER	Slater exchange (alpha=2/3)
	= BECKE	Becke's 1988 exchange
	= DEPRISTO	Depristo/Kress exchange
	= CAMA	Handy et al's mods to Becke exchange
	= HALF	50-50 mix of Becke and HF exchange correlation functionals:
	= VWN	Vosko/Wilke/Nusair correlation, formula 5
	= PWLOC	Perdew/Wang local correlation
	= LYP	Lee/Yang/Parr correlation exchange/correlation functionals:
	= BVWN	Becke exchange + VWN5 correlation
	= BLYP	Becke exchange + LYP correlation
	= BPWLOC	Becke exchange + Perdew/Wang correlation
	= B3LYP	hybridized HF/Becke/LYP using VWN formula 5
	= CAMB	CAMA exchange + Cambridge correlation
	= XVWN	Xalpha exchange + VWN5 correlation
	= XPWLOC	Xalpha exchange + Perdew/Wang correlation
	= SVWN	Slater exchange + VWN5 correlation
	= SPWLOC	Slater exchange + PWLOC correlation
	= WIGNER	Wigner exchange + correlation
	= WS	Wigner scaled exchange + correlation
	= WIGEXP	Wigner exponential exchange + correlation
AUXFUN	= AUX0	uses no auxiliary basis set for resolution of the identity, limiting accuracy.
	= AUX3	uses the 3rd generation of RI basis sets, These are available for the elements H to Ar, but have been carefully considered for H-Ne only. (DEFAULT)
THREE	=	a flag to use a resolution of the identity to turn four center overlap integrals into three center integrals. This can be used only if no auxiliary basis is employed. (default=.FALSE.)

\$MP2

\$MP2 group (relevant to SCFTYP=RHF,UHF,ROHF if MPLEVL=2)

Controls 2nd order Moller-Plesset perturbation runs, if requested by MPLEVL in \$CONTRL. See also the DIRSCF keyword in \$SCF to select direct MP2. MP2 is implemented for RHF, high spin ROHF, or UHF wavefunctions, but see also \$MCQDPT for MCSCF. Analytic gradients and the first order correction to the wavefunction (i.e. properties) are only available for RHF and UHF. The \$MP2 group is not usually given.

- NACORE = n Omits the first n occupied orbitals from the calculation. The default for n is the number of chemical core orbitals.
- NBCORE = Same as NACORE, for the beta orbitals of UHF. It is almost always the same value as NACORE.
- MP2PRP = a flag to turn on property computation for RHF or UHF MP2 jobs with RUNTYP=ENERGY. This is appreciably more expensive than just evaluating the 2nd order energy correction alone, so the default is .FALSE. Properties are always computed during gradient runs, when they are an almost free byproduct. (default=.FALSE.)
- LMOMP2 = a flag to analyze the closed shell MP2 energy in terms of localized orbitals. Any type of localized orbital may be used. This option is implemented only for RHF, and its selection forces use of the METHOD=3 transformation. The default is .FALSE.
- OSPT = selects open shell spin-restricted perturbation.
This parameter applies only when SCFTYP=ROHF. Please see the 'further information' section for more information about this choice.
- = ZAPT picks Z-averaged perturbation theory. (default)
- = RMP picks RMP (aka ROHF-MBPT) perturbation theory.
- CUTOFF = transformed integral retention threshold, the default is 1.0d-9.

The last 3 input variables apply to any serial MP2 run, or to parallel ROHF+MP2 runs using OSPT=RMP.

- NWORD = controls memory usage. The default uses all available memory.
(default=0)
- METHOD = n selects transformation method, 2 being the segmented transformation, and 3 being a more conventional two phase bin sort implementation. 3 requires more disk, but less memory. The default is to attempt method 2 first, and method 3 second.
- AOINTS = defines AO integral storage during conventional integral transformations, during parallel runs.
- DUP stores duplicated AO lists on each node, and is the default for parallel computers with slow interprocessor communication, e.g. ethernet.

DIST distributes the AO integral file across all nodes, and is the default for parallel computers with high speed communications.

\$CIS group

Required when CITYP=CIS

The CIS method (singly excited CI) is the simplest way to treat excited states. By Brillouin's Theorem, a single determinant reference such as RHF will have zero matrix elements with singly substituted determinants. The ground state reference therefore has no mixing with the excited states treated with singles only. Reading the references given in Section 4 of this manual will show the CIS method can be thought of as a non-correlated method, rigorously so for the ground state, and effectively so for the various excited states. Some issues making CIS rather less than a black box method are:

- a) any states characterized by important doubles are simply missing from the calculation.
- b) excited states commonly possess Rydberg (diffuse) character, so the AO basis used must allow this.
- c) excited states often have different point group symmetry than the ground state, so the starting geometries for these states must reflect their actual symmetry.
- d) excited state surfaces frequently cross, and thus root flipping may very well occur.

The implementation allows the use of only RHF references, but can pick up both singlet and triplet excited states. Nuclear gradients are available, as are properties.

NACORE = n Omits the first n occupied orbitals from the calculation. The default for n is the number of chemical core orbitals.

NSTATE = Number of states to be found (excluding the ground state).

ISTATE = State for which properties and/or gradient will be calculated. Only one state can be chosen.

HAMTYP = Type of CI Hamiltonian to use.
 = SAPS spin-adapted antisymmetrized product of the desired MULT will be used (default)
 = DETS determinant based, so both singlets and triplets will be obtained.

MULT = Multiplicity (1 or 3) of the singly excited SAPS (the reference is necessarily single RHF). Only relevant for SAPS based run.

DIAGZN = Hamiltonian diagonalization method.
 = DAVID use Davidson diagonalization. (default)
 = FULL construct the full matrix in memory and diagonalize, thus determining all states(not recommended except for small cases).

DGAPRX = Flag to control whether approximate diagonal elements of the CI Hamiltonian (based only on the orbital energies) are used in the Davidson algorithm. Note, this only affects the rate of convergence, not the resulting final energies. If set .FALSE., the exact diagonal elements are determined and used. Default=.TRUE.

NGSVEC = Dimension of the Hamiltonian submatrix that is diagonalized to form the initial CI vectors. The default is the greater of NSTATE*2 and 10.

- \$CISVEC group required if RDCISV in \$CIS is chosen

This is formatted data generated by a previous CIS run, to be read back in as starting vectors. Sometimes molecular orbital phase changes make these CI vectors problematic.

\$CCINP group (optional, relevant for any CCTYP)

This group controls a coupled-cluster calculation of the type specified by CCTYP in \$CONTRL. If omitted, all valence electrons will be correlated. See the "Further Information" section of this manual for more details.

- NCORE = gives the number of frozen core orbitals to be omitted from the CC calculation. The default is the number of chemical core orbitals.
- NFZV = the number of frozen virtual orbitals to be omitted from the calculation. The default is 0.
- MAXCC = defines the maximum number of CCSD (or LCCD, CCD) iterations. The default is 30.
- ICONV = defines the convergence criterion for the cluster amplitudes. CC iterations are converged when the maximum change in amplitudes is less than $10^{*(-ICONV)}$. The default is 7.
- NWORD = a limit on memory to be used in the CC steps. The default is 0, meaning all memory available will be used.
- IREST = defines the restart option. If the value of IREST is greater or equal 3, program will restart from the earlier CC run. This requires saving the disk file CCREST from the previous CC run. Values of IREST between 0 and 3 should not be used. In general, the value of IREST is used by the program to set the iteration counter in the restarted run. The default is 0, meaning no restart is attempted.
- MXDIIS = defines the number of cluster amplitude vectors from previous iterations to be included in the DIIS extrapolation during the CCSD (or LCCD, CCD) iterative process. The default value of MXDIIS is 5 for all but small problems. The DIIS solver can be disengaged by entering MXDIIS = 0. It is not necessary to change the default value of MXDIIS, unless the CC equations do not converge in spite of increasing the value of MAXCC.
- AMPTSH = defines a threshold for eliminating small cluster amplitudes from the CC calculations. Amplitudes with absolute values smaller than AMPTSH are set to zero. The default is to retain all small amplitudes, meaning fully accurate CC iterations. Default = 0.0.

\$GUESS

\$GUESS group (optional, relevant for all SCFTYP's)

This group controls the selection of initial molecular orbitals.

GUESS	=	Selects type of initial orbital guess.
= HUCKEL		Carry out an extended Huckel calculation using a Huzinaga MINI basis set, and project this onto the current basis. This is implemented for atoms up to Rn, and will work for any all electron or ECP basis set. (default for most runs)
= HCORE		Diagonalize the one electron Hamiltonian to obtain the initial guess orbitals. This method is applicable to any basis set, but does not work as well as the HUCKEL guess.
= MOREAD		Read in formatted vectors punched by an earlier run. This requires a \$VEC group, and you MUST pay attention to NORB below.
= RDMINI		Read in a \$VEC group from a converged calculation that used GBASIS=MINI and no polarization functions, and project these orbitals onto the current basis. Do not use this option if the current basis involve ECP basis sets.
= MOSAVED		(default for restarts) The initial orbitals are read from the DICTNRY file of the earlier run.
= SKIP		Bypass initial orbital selection. The initial orbitals and density matrix are assumed to be in the DICTNRY file. Mostly used for RUNTYP=HESSIAN when the hessian is being read in from the input.

All GUESS types except 'SKIP' permit reordering of the orbitals, carry out an orthonormalization of the orbitals, and generate the correct initial density matrix, for RHF, UHF, ROHF, and GVB, but note that correct computation of the GVB density requires also CICOEF in \$SCF. The density matrix cannot be generated from the orbitals alone for MP2, CI, or MCSCF, so property evaluation for these should be RUNTYP=ENERGY rather than RUNTYP=PROP using GUESS=MOREAD.

PRTMO = a flag to control printing of the initial guess. (default=.FALSE.)

PUNMO = a flag to control punching of the initial guess. (default=.FALSE.)

MIX = rotate the alpha and beta HOMO and LUMO orbitals so as to generate inequivalent alpha and beta orbital spaces. This pertains to UHF singlets only. This may require use of NOSYM=1 in \$CONTRL depending on your situation. (default=.FALSE.)

NORB = The number of orbitals to be read in the \$VEC group. This applies only to GUESS=MOREAD.

For -RHF-, -UHF-, -ROHF-, and -GVB-, NORB defaults to the number of occupied orbitals. NORB must be given for -CI- and -MCSCF-. For -UHF-, if NORB is not given, only the occupied alpha and beta orbitals should be given, back to back. Otherwise, both alpha and beta orbitals must consist of NORB vectors. NORB may be larger than the number of occupied MOs, if you wish to read in the virtual orbitals. If NORB is less than the number of atomic orbitals, the remaining orbitals are generated as the orthogonal complement to those read.

- NORDER = Orbital reordering switch.
 = 0 No reordering (default)
 = 1 Reorder according to IORDER and JORDER.
- IORDER = Reordering instructions.
 Input to this array gives the new molecular orbital order. For example, IORDER(3)=4,3 will interchange orbitals 3 and 4, while leaving the other MOs in the original order. This parameter applies to all orbitals (alpha and beta) except for -UHF-, where it only affects the alpha MOs. (default is IORDER(i)=i)
- JORDER = Reordering instructions.
 Same as IORDER, but for the beta MOs of -UHF-.
- INSORB = the first INSORB orbitals specified in the \$VEC group will be inserted into the Huckel guess, making the guess a hybrid of HUCKEL/MOREAD. This keyword is meaningful only when GUESS=HUCKEL, and it is useful mainly for QM/MM runs where some orbitals (buffer) are frozen and need to be transferred to the initial guess vector set, see \$MOFRZ. (default=0)
- * * * the next are 3 ways to clean up orbitals * * *
- PURIFY = flag to symmetrize starting orbitals. This is the most soundly based of the possible procedures. However it may fail in complicated groups when the orbitals are very unsymmetric. (default=.FALSE.)
- TOLZ = level below which MO coefficients will be set to zero. (default=1.0E-7)
- TOLE = level at which MO coefficients will be equated. This is a relative level, coefficients are set equal if one agrees in magnitude to TOLE times the other. (default=5.0E-5)
- SYMDEN = project the initial density in order to generate symmetric orbitals. This may be useful if the HUCKEL or HCORE guess types give orbitals of impure symmetry (?s present). The procedure will generate a fairly high starting energy, and thus its use may not be a good idea for orbitals of the quality of MOREAD. (default=.FALSE.)

\$VEC, \$MOFRZ

\$VEC group (optional, relevant for all SCFTYP's)
 (required if GUESS=MOREAD)

This group consists of formatted vectors, as written onto file PUNCH in a previous run. It is considered good form to retain the titling comment cards punched before the \$VEC card, as a reminder to yourself of the origin of the orbitals.

For Morokuma decompositions, the names of this group are \$VEC1, \$VEC2, ... for each monomer, computed in the identical orientation as the supermolecule. For transition moment or spin-orbit coupling runs, orbitals for states one and possibly two are \$VEC1 and \$VEC2.

\$MOFRZ group (optional, relevant for RHF, ROHF, GVB)

This group controls freezing the molecular orbitals of your choice during the SCF procedure. If you choose this option, select DIIS in \$SCF since SOSCF will not converge as well. GUESS=MOREAD is required in \$GUESS.

FRZ = flag which triggers MO freezing. (default=.FALSE.)

IFRZ = an array of MOs in the input \$VEC set which are to be frozen. There is no default for this.

\$STATPT group (optional, for RUNTYP=OPTIMIZE or SADPOINT)

This group controls the search for stationary points. Note that NZVAR in \$CONTRL determines if the geometry search is conducted in Cartesian or internal coordinates.

METHOD = optimization algorithm selection. Pick from

NR	Straight Newton-Raphson iterate. This will attempt to locate the nearest stationary point, which may be of any order. There is no steplength control. RUNTYP can be either OPTIMIZE or SADPOINT
RFO	Rational Function Optimization. This is one of the augmented Hessian techniques where the shift parameter(s) is(are) chosen by a rational function approximation to the PES. For SADPOINT searches it involves two shift parameters. If the calculated stepsize is larger than DXMAX the step is simply scaled down to size.
QA	Quadratic Approximation. This is another version of an augmented Hessian technique where the shift parameter is chosen such that the steplength is equal to DXMAX. It is completely equivalent to the TRIM method. (default)
SCHLEGEL	The quasi-NR optimizer by Schlegel.
CONOPT	CONstrained OPTimization. An algorithm which can be used for locating TSS. The starting geometry MUST be a minimum! The algorithm tries to push the geometry uphill along a chosen Hessian mode (IFOLLOW) by a series of optimizations on hyperspheres of increasingly larger radii. Note that there currently are no restart capabilities for this method, not even manually.

OPTTOL = gradient convergence tolerance, in Hartree/Bohr. Convergence of a geometry search requires the largest component of the gradient to be less than OPTTOL, and the root mean square gradient less than 1/3 of OPTTOL. (default=0.0001)

NSTEP = maximum number of steps to take. Restart data is punched if NSTEP is exceeded. (default=20)

- the next four control the step size

DXMAX = initial trust radius of the step, in Bohr.
 For METHOD=RFO, QA, or SCHLEGEL, steps will be scaled down to this value, if necessary. (default=0.3 for OPTIMIZE and 0.2 for SADPOINT)
 For METHOD=NR, DXMAX is inoperative.
 For METHOD=CONOPT, DXMAX is the step along the previous two points to increment the hypersphere radius between constrained optimizations. (default=0.1)

- the next three apply only to METHOD=RFO or QA:

TRUPD = a flag to allow the trust radius to change as the geometry search proceeds. (default=.TRUE.)

TRMAX = maximum permissible value of the trust radius. (default=0.5 for OPTIMIZE and 0.3 for SADPOINT)

TRMIN = minimum permissible value of the trust radius. (default=0.05)

- the next three control mode following

IFOLLOW = Mode selection switch, for RUNTYP=SADPOINT.
For METHOD=RFO or QA, the mode along which the energy is maximized, other modes are minimized. Usually referred to as "eigenvector following".
For METHOD=Schlegel, the mode whose eigenvalue is (or will be made) negative. All other curvatures will be made positive.
For METHOD=CONOPT, the mode along which the geometry is initially perturbed from the minima. (default is 1)
In Cartesian coordinates, this variable doesn't count the six translation and rotation degrees. Note that the "modes" aren't from mass-weighting.

STPT = flag to indicate whether the initial geometry is considered a stationary point. If .true. the initial geometry will be perturbed by a step along the IFOLLOW normal mode with stepsize STSTEP. (default=.false.) The positive direction is taken as the one where the largest component of the Hessian mode is positive. If there are more than one largest component (symmetry), the first is taken as positive.
Note that STPT=.TRUE. has little meaning with HESS=GUESS as there will be many degenerate eigenvalues.

STSTEP = Stepsize for jumping off a stationary point. Using values of 0.05 or more may work better. (default=0.01)

IFREEZ = array of coordinates to freeze. These may be internal or Cartesian coordinates. For example, IFREEZ(1)=1,3 freezes the two bond lengths in the \$ZMAT example, while optimizing the angle. If NZVAR=0, so that this value applies to the Cartesian coordinates instead, the input of IFREEZ(1)=4,7 means to freeze the x coordinates of the 2nd and 3rd atoms in the molecule.

See also IFZMAT and FVALUE in \$ZMAT, and IFCART below, as IFREEZ does not apply to DLC internals.

In a numerical Hessian run, IFREEZ specifies Cartesian displacements to be skipped for a Partial Hessian Analysis. For more information:
J.D.Head, Int.J.Quantum Chem. 65, 827, 1997
H.Li, J.H.Jensen Theoret. Chem. Acc. 107, 211-219(2002)

IFCART = array of Cartesian coordinates to freeze during a geometry optimization using delocalized internal coordinates.

- The next two control the hessian matrix quality

HESS = selects the initial hessian matrix.
 = GUESS chooses a positive definite diagonal hessian. (default for RUNTYP=OPTIMIZE)
 = READ causes the hessian to be read from a \$HESS group. (default for RUNTYP=SADPOINT)
 = RDAB reads only the ab initio part of the hessian, and approximates the effective fragment blocks.
 = RDALL reads the full hessian, then converts any fragment blocks to 6x6 T+R shape. (this option is seldom used).
 = CALC causes the hessian to be computed, see the \$FORCE group.

 IHREP = the number of steps before the hessian is recomputed. If given as 0, the hessian will be computed only at the initial geometry if you choose HESS=CALC, and never again. If nonzero, the hessian is recalculated every IHREP steps, with the update formula used on other steps. (default=0)

- the next two control the amount of output

Let 0 mean the initial geometry, L mean the last geometry, and all mean every geometry. Let INTR mean the internuclear distance matrix. Let HESS mean the approximation to the hessian. Note that a directly calculated hessian matrix will always be punched, NPUN refers only to the updated Hessians used by the quasi-Newton step.

NPRT = 1 Print INTR at all, orbitals at all
 0 Print INTR at all, orbitals at O+L (default)
 -1 Print INTR at all, orbitals never
 -2 Print INTR at O+L, orbitals never

 NPUN = 3 Punch all orbitals and HESS at all
 2 Punch all orbitals at all
 1 same as 0, plus punch HESS at all
 0 Punch all orbitals at O+L, otherwise only occupied orbitals (default)
 -1 Punch occ orbitals at O+L only
 -2 Never punch orbitals

 HSEND = a flag to control automatic hessian evaluation at the end of a successful geometry search. (default=.FALSE.)

--- the following parameters are quite specialized ---

PURIFY = a flag to help eliminate the rotational and translational degrees of freedom from the initial hessian (and possibly initial gradient). This is much like the variable of the same name in \$FORCE, and will be relevant only if internal coordinates are in use. (default=.FALSE.)

- PROJECT = a flag to eliminate translation and rotational degrees of freedom from Cartesian optimizations. The default is .TRUE. since this normally will reduce the number of steps, except that this variable is set false when POSITION=FIXED is used during EFP runs.
- ITBMAT = number of micro-iterations used to compute the step in Cartesians which corresponds to the desired step in internals. The default is 5.
- UPHESS = SKIP do not update Hessian (not recommended)
 BFGS default for OPTIMIZE using RFO or QA
 POWELL default for OPTIMIZE using NR or CONOPT
 POWELL default for SADPOINT
 MSP mixed Murtagh-Sargent/Powell update
 SCHLEGEL only choice for METHOD=Schlegel
- MOVIE = a flag to create a series of structural data which can be show as a movie by the Macintosh program Chem3D. The data is written to the file IRCDATA. (default=.FALSE.)

- - - - NNEG, RMIN, RMAX, RLIM apply only to Schlegel - - - -

- NNEG = The number of negative eigenvalues the force constant matrix should have. If necessary the smallest eigenvalues will be reversed. The default is 0 for RUNTYP=OPTIMIZE, and 1 for RUNTYP=SADPOINT.
- RMIN = Minimum distance threshold. Points whose root mean square distance from the current point is less than RMIN are discarded. (default=0.0015)
- RMAX = Maximum distance threshold. Points whose root mean square distance from the current point is greater than RMAX are discarded. (default=0.1)
- RLIM = Linear dependence threshold. Vectors from the current point to the previous points must not be collinear. (default=0.07)

- See the 'further information' section for some help with OPTIMIZE and SADPOINT runs

\$TRUDGE group (optional, required for RUNTYP=TRUDGE)

This group defines the parameters for a non-gradient optimization of exponents or the geometry. The TRUDGE package is a modified version of the same code from Michel Dupuis' HONDO 7.0 system, originally written by H.F.King. Presently the program allows for the optimization of 10 parameters.

Exponent optimization works only for uncontracted primitives, without enforcing any constraints. Two non-symmetry equivalent H atoms would have

their p function exponents optimized separately, and so would two symmetry equivalent atoms! A clear case of GIGO.

Geometry optimization works only in HINT internal coordinates (see \$CONTRL and \$DATA groups). The total energy of all types of SCF wavefunctions can be optimized, although this would be extremely stupid as gradient methods are far more efficient. The main utility is for open shell MP2 or CI geometry optimizations, which may not be done in any other way with GAMESS. If your run requires NOSYM=1 in \$CONTRL, you must be sure to use only C1 symmetry in the \$DATA group.

OPTMIZ = a flag to select optimization of either geometry or exponents of primitive gaussian functions.
 = BASIS for basis set optimization.
 = GEOMETRY for geometry optimization (default). This means minima search only, there is no saddle point capability.

NPAR = number of parameters to be optimized.

IEX = defines the parameters to be optimized.

If OPTMIZ=BASIS, IEX declares the serial number of the Gaussian primitives for which the exponents will be optimized.

If OPTMIZ=GEOMETRY, IEX define the pointers to the HINT internal coordinates which will be optimized. (Note that not all internal coordinates have to be optimized.) The pointers to the internal coordinates are defined as: (the number of atom on the input list)*10 + (the number of internal coordinate for that atom). For each atom, the HINT internal coordinates are numbered as 1, 2, and 3 for BOND, ALPHA, and BETA, respectively.

P = Defines the initial values of the parameters to be optimized. You can use this to reset values given in \$DATA. If omitted, the \$DATA values are used. If given here, geometric data must be in Angstroms and degrees.

A complete example is a TCSCF multireference 6-31G geometry optimization for methylene,

```

$CONTRL SCFTYP=GVB CITYP=GUGA RUNTYP=TRUDGE
        COORD=HINT $END
$BASIS  GBASIS=N31 NGAUSS=6 $END
$DATA
Methylene TCSCF+CISD geometry optimization
Cnv 2

C    6.    LC  0.00  0.0  0.00  -  0  K
H    1.    PCC 1.00  53.  0.00  +  0  K  I
$END
$SCF     NCO=3 NPAIR=1 $END
$TRUDGE OPTMIZ=GEOMETRY NPAR=2
        IEX(1)=21, 22 P(1)=1.08 $END
$CIDRT  GROUP=C2V SOCI=. TRUE. NFZC=1 NDOC=3 NVAL=1
        NEXT=- 1 $END

```

using GVB-PP(1), or TCSCF orbitals in the CI. The starting bond length is reset to 1.09, while the initial angle will be 106 (twice 53). Result after 17 steps is R=1.1283056, half-angle=51.83377, with a CI energy of -38.9407538472

Note that you may optimize the geometry for an excited CI state, just specify

\$GUGDIA NSTATE=5 \$END

\$GUGDM IROOT=3 \$END

to find the equilibrium geometry of the third state (of five total states) of the symmetry implied by your \$CIDRT.

\$TRURST group (optional, relevant for RUNTYP=TRUDGE)

This group specifies restart parameters for TRUDGE runs and accuracy thresholds.

KSTART indicates the conjugate gradient direction in which the optimization will proceed. (default = -1)
 -1 indicates that this is a non-restart run.
 0 corresponds to a restart run.

FNOISE accuracy of function values. Variation smaller than FNOISE are not considered to be significant (Def. 0.0005)

TOLF accuracy required of the function (Def. 0.001)

TOLR accuracy required of conjugate directions (Def. 0.05)

For geometry optimization, the values which give better results (closer to the ones obtained with gradient methods) are: TOLF=0.0001, TOLR=0.001, FNOISE=0.00001

\$FORCE group
 (optional, relevant for RUNTYP=HESSIAN,OPTIMIZE,SADPOINT)

This group controls the computation of the hessian matrix (the energy second derivative tensor, also known as the force constant matrix), and an optional harmonic vibrational analysis. This can be a very time consuming calculation. However, given the force constant matrix, the vibrational analysis for an isotopically substituted molecule is very cheap. Related input is HESS= in \$STATPT, and the \$MASS, \$HESS, \$GRAD, \$DIPDR, \$VIB groups.

METHOD = chooses the computational method.
 = **ANALYTIC** is implemented only for SCFTYPs RHF, ROHF, and GVB (when NPAIR is 0 or 1). This is the default for these cases.
 = **NUMERIC** is the default for all other cases: UHF or MCSCF, RESC or NESC relativistic correction, and all MP2, CI, or DFT runs.

RDHESS = a flag to read the hessian from a \$HESS group, rather than computing it. This variable pertains only to RUNTYP=HESSIAN. See also HESS= in the \$STATPT group. (default is .FALSE.)

PURIFY = controls cleanup
 Given a \$ZMAT, the hessian and dipole derivative tensor can be "purified" by transforming from Cartesians to internals and back to Cartesians. This effectively zeros the frequencies of the translation and rotation "modes", along with their IR intensities. The purified quantities are punched out. Purification does change the Hessian slightly, frequencies at a stationary point can change by a wave number or so. The change is bigger at non-stationary points. (default=.FALSE. if \$ZMAT is given)

PRTIFC = prints the internal coordinate force constants. You MUST have defined a

\$FORCE

\$ZMAT group to use this. (Default=.FALSE.)

--- the next four apply only to METHOD=NUMERIC ---

NVIB = Number of displacements in each Cartesian direction for force field computation.

= 1 Move one VIBSIZ unit in each positive Cartesian direction. This requires $3N+1$ evaluations of the wavefunction, energy, and gradient, where N is the number of SYMMETRY UNIQUE atoms given in \$DATA. (default)

= 2 Move one VIBSIZ unit in the positive direction and one VIBSIZ unit in the negative direction. This requires $6N+1$ evaluations of the wavefunction and gradient, and gives a small improvement in accuracy. In particular, the frequencies will change from NVIB=1 results by no more than 10-100 wavenumbers, and usually much less. However, the normal modes will be more nearly symmetry adapted, and the residual rotational and translational "frequencies" will be much closer to zero.

VIBSIZ = Displacement size (in Bohrs). Default=0.01

Let O mean the Vib0 geometry, and D mean all the displaced geometries

NPRT = 1 Print orbitals at O and D
 = 0 Print orbitals at O only (default)

NPUN = 2 Punch all orbitals at O and D
 = 1 Punch all orbitals at O and occupied orbs at D
 = 0 Punch all orbitals at O only (default)

----- the rest control normal coordinate analysis -----

VIBANL = flag to activate vibrational analysis.
 (the default is .TRUE. for RUNTYP=HESSIAN, and otherwise is .FALSE.)

SCLFAC = scale factor for vibrational frequencies, used in calculating the zero point vibrational energy. Some workers correct for the usual overestimate in SCF frequencies by a factor 0.89. ZPE or other methods might employ other factors, see A.P.Scott, L.Radom J.Phys.Chem. 100, 16502-16513 (1996). The output always prints unscaled frequencies, so this value is used only during the thermochemical analysis.(Default is 1.0)

TEMP = an array of up to ten temperatures at which the thermochemistry should be printed out. The default is a single temperature, 298.15 K. To use absolute zero, input 0.001 degrees.

FREQ = an array of vibrational frequencies. If the frequencies are given here, the hessian matrix is not computed or read. You enter any imaginary frequencies as negative numbers, omit the zero frequencies corresponding to translation and rotation, and enter all true vibrational frequencies. Thermodynamic properties will be printed, nothing else is done by the run.

- PRTSCN = flag to print contribution of each vibrational mode to the entropy.
(Default is .FALSE.)
- DECOMP = activates internal coordinate analysis. Vibrational frequencies will be decomposed into "intrinsic frequencies", by the method of J.A.Boatz and M.S.Gordon, J.Phys.Chem., 93, 1819-1826(1989). If set .TRUE., the \$ZMAT group may define more than 3N-6 (3N-5) coordinates.
(default=.FALSE.)
- PROJCT = controls the projection of the hessian matrix.
The projection technique is described by W.H.Miller, N.C.Handy, J.E.Adams in J. Chem. Phys. 1980 , 72, 99-112. At stationary points, the projection simply eliminates rotational and translational contaminants. At points with non-zero gradients, the projection also ensures that one of the vibrational modes will point along the gradient, so that there are a total of 7 zero frequencies. The other 3N-7 modes are constrained to be orthogonal to the gradient. Because the projection has such a large effect on the hessian, the hessian punched is the one BEFORE projection. For the same reason, the default is .FALSE. to skip the projection, which is mainly of interest in dynamical calculations.
-
-

There is a set of programs for the calculation of kinetic or equilibrium isotope effects from the group of Piotr Paneth at the University of Lodz. This ISOEFF package will accept data computed by GAMESS, and can be downloaded at <http://ck-sg.p.lodz.pl/isoeff/isoeff.html>

\$CPHF, \$HESS

\$CPHF group (relevant for analytic RUNTYP=HESSIAN)

This group controls the solution of the response equations, also known as coupled Hartree-Fock.

POLAR = a flag to request computation of the static polarizability, alpha. Because this property needs 3 additional response vectors, beyond those needed for the hessian, the default is to skip the property. (default = .FALSE.)

NWORD = controls memory usage for this step. The default uses all available memory. (default=0)

\$HESS group (relevant for RUNTYP=HESSIAN if RDHESS=.TRUE.)
 (relevant for RUNTYP=IRC if FREQ,CMODE not given)
 (relevant for RUNTYP=OPTIMIZE,SADPOINT if HESS=READ)

Formatted force constant matrix (FCM), i.e. hessian matrix. This data is punched out by a RUNTYP=HESSIAN job, in the correct format for subsequent runs. The first card in the group must be a title card.

A \$HESS group is always punched in Cartesians. It will be transformed into internal coordinate space if a geometry search uses internals. It will be mass weighted (according to \$MASS) for IRC and frequency runs.

The initial FCM is updated during the course of a geometry optimization or saddle point search, and will be punched if a run exhausts its time limit. This allows restarts where the job leaves off. You may want to read this FCM back into the program for your restart, or you may prefer to regenerate a new initial hessian. In any case, this updated hessian is absolutely not suitable for frequency prediction!

\$GRAD group (relevant for RUNTYP=OPTIMIZE or SADPOINT)
 (relevant for RUNTYP=HESSIAN when RDHESS=.TRUE.)

Formatted gradient vector at the \$DATA geometry. This data is read in the same format it was punched out.

For RUNTYP=HESSIAN, this information is used to determine if you are at a stationary point, and possibly for projection. If omitted, the program pretends the gradient is zero, and otherwise proceeds normally.

For geometry searches, this information (if known) can be read into the program so that the first step can be taken instantly.

\$DIPDR group (relevant for RUNTYP=HESSIAN if RDHESS=.T.)

Formatted dipole derivative tensor, punched in a previous RUNTYP=HESSIAN job. If this group is omitted, then a vibrational analysis will be unable to predict the IR intensities, but the run can otherwise proceed.

\$VIB group (relevant for RUNTYP=HESSIAN, METHOD=NUMERIC)

Formatted card image -restart- data. This data is read in the format it was punched by a previous HESSIAN job to the file IRCDATA. Just add a " \$END" card, and if the final gradient was punched as zero, delete the last set of data. Normally, IREST in \$CONTRL will NOT be used in conjunction with a HESSIAN restart. The mere presence of this deck triggers the restart from cards. This deck can also be used to turn a single point differencing run into double differencing, as well as recovering from time limits, or other bombouts.

\$MASS group (relevant for RUNTYP=HESSIAN, IRC, or DRC)

This group permits isotopic substitution during the computation of mass weighted Cartesian coordinates. Of course, the masses affect the frequencies and normal modes of vibration.

AMASS = An array giving the atomic masses, in amu. The default is to use the mass of the most abundant isotope. Masses through element 104 are stored.

example - \$MASS AMASS(3)=2.0140 \$END
 will make the third atom in the molecule a deuterium.

\$IRC group (relevant for RUNTYP=IRC)

This group governs the location of the intrinsic reaction coordinate, a steepest descent path in mass weighted coordinates, that connects the saddle point to reactants and products.

- - - - there are five integration methods chosen by PACE.

PACE = GS2 selects the Gonzalez-Schlegel second order method. This is the default method.

Related input is:

GCUT	cutoff for the norm of the mass-weighted gradient tangent (the default is chosen in the range from 0.00005 to 0.00020, depending on the value for STRIDE chosen below.
RCUT	cutoff for Cartesian RMS displacement vector. (the default is chosen in the range 0.0005 to 0.0020 Bohr, depending on the value for STRIDE)
ACUT	maximum angle from end points for linear interpolation (default=5 degrees)
MXOPT	maximum number of constrained optimization steps for each IRC point (default=20)
IHUPD	is the hessian update formula. 1 means Powell, 2 means BFGS (default=2)
GA	is a gradient from the previous IRC point, and is used when restarting.
OPTTOL	is a gradient cutoff used to determine if the IRC is approaching a minimum. It has the same meaning as the variable in \$STATPT. (default=0.0001)

PACE = LINEAR selects linear gradient following (Euler's method).

Related input is:

STABLZ	switches on Ishida/Morokuma/Komornicki reaction path stabilization. The default is .TRUE.
DELTA	initial step size along the unit bisector, if STABLZ is on. Default=0.025 Bohr.
ELBOW	is the collinearity threshold above which the stabilization is skipped. If the mass weighted gradients at QB and QC are almost collinear, the reaction path is deemed to be curving very little, and stabilization isn't needed. The default is 175.0 degrees. To always perform stabilization, input 180.0.
READQB,EB,GBNORM,GB	are energy and gradient data already known at the current IRC point. If it happens that a run with STABLZ on decides to skip stabilization because of ELBOW, this data will be punched to speed the restart.

PACE = QUAD selects quadratic gradient following.
Related input is:

SAB distance to previous point on the IRC.
GA gradient vector at that historical point.

PACE = AMPC4 selects the fourth order Adams-Moulton variable step predictor-corrector.

Related input is:

GA0,GA1,GA2 which are gradients at previous points.

PACE = RK4 selects the 4th order Runge-Kutta variable step method.
There is no related input.

- - - - - The next two are used by all PACE choices - - - - -

STRIDE = Determines how far apart points on the reaction path will be. STRIDE is used to calculate the step taken, according to the PACE you choose. The default is good for the GS2 method, which is very robust. Other methods should request much smaller step sizes, such as 0.10 or even 0.05. (default = $0.30 \sqrt{\text{amu}} \cdot \text{Bohr}$)

NPOINT = The number of IRC points to be located in this run. The default is to find only the next point. (default = 1)

- - - - - The next two let you choose your output volume - - - - -

Let F mean the first IRC point found in this run, and L mean the final IRC point of this run. Let INTR mean the internuclear distance matrix.

NPRT = 1 Print INTR at all, orbitals at all IRC points
0 Print INTR at all, orbitals at F+L (default)
-1 Print INTR at all, orbitals never
-2 Print INTR at F+L, orbitals never

NPUN = 1 Punch all orbitals at all IRC points
0 Punch all orbitals at F+L, only occupied orbitals at IRC points between (default)
-1 Punch all orbitals at F+L only
-2 Never punch orbitals

- The next two tally the reaction path results. The defaults are appropriate for starting from a saddle point, restart values are automatically punched out.

NEXTPT = The number of the next point to be computed.

STOTAL = Total distance along the reaction path to next IRC point, in mass weighted Cartesian space.

- The following controls jumping off the saddle point. If you give a \$HESS group, \$FREQ and \$CMODE will be generated automatically.

SADDLE = A logical variable telling if the coordinates given in the \$DATA deck are at

a saddle point (.TRUE.) or some other point lying on the IRC (.FALSE.). If SADDLE is true, either a \$HESS group or else FREQ and CMODE must be given. (default = .FALSE.)

Related input is:

- TSENGY = A logical variable controlling whether the energy and wavefunction are evaluated at the transition state coordinates given in \$DATA. Since you already know the energy from the transition state search and force field runs, the default is .F.
- FORWRD = A logical variable controlling the direction to proceed away from a saddle point. The forward direction is defined as the direction in which the largest magnitude component of the imaginary normal mode is positive. (default = .TRUE.)
- EVIB = Desired decrease in energy when following the imaginary normal mode away from a saddle point. (default=0.0005 Hartree)
- FREQ = The magnitude of the imaginary frequency, given in cm^{-1} .
- CMODE = An array of the components of the normal mode whose frequency is imaginary, in Cartesian coordinates. Be careful with the signs!

You must give FREQ and CMODE if you don't give a \$HESS group, when SADDLE=.TRUE. The option of giving these two variables instead of a \$HESS does not apply to the GS2 method, which must have a hessian input, even for restarts. Note also that EVIB is ignored by GS2 runs.

- For hints about IRC tracking, see the 'further information' section.

\$VSCF group (optional, relevant to RUNTYP=VSCF)

This group governs the computation of frequencies including anharmonic effects. Besides the values shown below, the input file must contain a \$HESS group and perhaps a \$DIPDR group, to start with previously obtained harmonic vibrational information. Energies are sampled along the directions of harmonic normal modes, and along pairs of harmonic normal modes, after which vibrational nuclear wavefunctions are obtained at an SCF-like level, termed VSCF, using product nuclear wavefunctions. An MP2-like correction to the vibrational energy, termed correlation corrected (cc-VSCF), is also obtained. In addition, degenerate perturbation theory is performed, based on a CI reference that includes linear combinations of degenerate states. By default, the dipole is computed at every grid point to give improved IR intensity values. See also the restart group \$VIBSCF.

NGRID = number of grid points to be computed along each harmonic normal mode, and if NCOUP=2, along each pair of modes. Reasonable values are 8 or 16, with 16 considered significantly more accurate. (default=16)

NCOUP = the order of mode couplings included.
 = 1 computes 1-D grids along each harmonic mode
 = 2 adds additionally, 2-D grids along each pair of normal modes. (default)

The total number of energy and dipole evaluations for NCOUP=2 is $M \cdot \text{NGRID} + M \cdot (M-1)/2 \cdot \text{NGRID}^2$, where M is the number of normal modes: $M = 3N-6$ or $3N-5$.

The next five relate to the solver for the vibrational states. The default is a degenerate perturbation theory treatment including the ground and every singly excited vibrational level.

VDPT = flag to use 2nd order degenerate perturbation theory to find vibrational energys. Turning this off causes only a CI singles and doubles treatment to be made. (default=.true.)

ICASX = vibrational excitation level to include in the solver's basis. 1,2... mean first, second... excitations will be included. The default, 1, includes single quantum excited states only.

ICAS1, ICAS2 = starting and ending vibrations whose quanta are included, according to ICASX. The default is all modes, ICAS1=1 and ICAS2=3N-6.

SFACT = a numerical cutoff for small contributions in the solver. The default is $1d-5$.

CASMIN = a flag, largely redundant, that ensures defaultsettings for ICAS1 and ICAS2

The solver finds the ground state ($v=0$) by default, but will readily find excited levels (such as all $v=1$) if restarted. Note that IEXC is one greater than the sum of the vibrational quantum numbers.

IEXC = 1 obtain fundamental frequencies (default)
 = 2 instead, obtain first overtones

\$VSCF, \$VIBSCF

= instead, obtain second overtones

IEXC higher than 1 may be speedily obtained using the next parameter to restart with a completed \$VIBSCF group.

READV = flag to indicate restart data \$VIBSCF should be read in to resume an interrupted calculation, or to obtain overtones in follow-on runs. (default is .FALSE.)

IMODE = array of modes for which anharmonic effects will be computed. IMODE(1)=10,19 computes anharmonic energies and wavefunctions for modes 10 and 19, only. In the current implementation, pairs of modes cannot be coupled, so NCOUP is forced to 1 if this option is specified.

PROJECT = controls the projection of the hessian matrix (same meaning as in \$FORCE). Default is .FALSE., but is .TRUE. if IFREEZ is specified in \$STATPT.

The next two relate to simplified intensity computation. These simplifications are aimed at speeding up MP2 runs, if one cares not so much about intensities, and so would like to reduce CPU for computing dipoles. It is pointless to select DMDR for SCF electronic structure, where the dipoles are easily obtainable. DMDR must not be used if overtones are being computed.

DMDR = if true, indicates that the harmonic dipole derivative tensor \$DIPDR is input, rather than computing the dipoles. (default is .FALSE.)

MPDIP = for MP2 electronic structure, a value of .FALSE. uses SCF level dipoles in order to save the time needed to obtain the MP2 density at every grid point. It is more accurate to use the DMDR flag instead of this option, if \$DIPDR is available. Obviously this variable is irrelevant for SCF level electronic structure. (default=.TRUE.)

= scaling factor for pair-coupling potential. Sometimes when pair-coupling potential values are larger than the corresponding single mode values, they must be scaled down. (Default=1.0)

=====

\$VIBSCF group (optional, relevant to RUNTYP=VSCF)

This is restart data, as written to file IRCDATA in a partially completed previous run. Append a " \$END" line, and select READV=.TRUE. to read the data.

=====

\$GRADEX group (optional, for RUNTYP=GRADEXTR)

This group controls the gradient extremal following algorithm. The GEs leave stationary points parallel to each of the normal modes of the hessian. Sometimes a GE leaving a minimum will find a transition state, and thus provides us with a way of finding that saddle point. GEs have many unusual mathematical properties, and you should be aware that they normally differ a great deal from IRCs.

The search will always be performed in cartesian coordinates, but internal coordinates along the way may be printed by the usual specification of NZVAR and \$ZMAT.

- METHOD = algorithm selection.
- SR A predictor-corrector method due to Sun and Ruedenberg (default).
 - JJH A method due to Jorgensen, Jensen and Helgaker.
- NSTEP = maximum number of predictor steps to take. (default=50)
- DPRED = the stepsize for the predictor step. (default = 0.10)
- STPT = a flag to indicate whether the initial geometry is considered a stationary point. If .TRUE., the geometry will be perturbed by STSTEP along the IFOLOW normal mode. (default = .TRUE.)
- STSTEP = the stepsize for jumping away from a stationary point. (default = 0.01)
- IFOLOW = Mode selection option. (default is 1)
 If STPT=.TRUE., the initial geometry will be perturbed by STSTEP along the IFOLOW normal mode. Note that IFOLOW can be positive or negative, depending on the direction the normal mode should be followed in. The positive direction is defined as the one where the largest component of the Hessian eigenvector is positive.
- If STPT=.FALSE. the sign of IFOLOW determines which direction the GE is followed in. A positive value will follow the GE in the uphill direction. The value of IFOLOW should be set to the Hessian mode which is parallel to the gradient to avoid miscellaneous warning messages.
- GOFIRST = a flag to indicate whether the algorithm should attempt to locate a stationary point. If .TRUE., a straight NR search is performed once the NR step length drops below SNRMAX. 10 NR step are then allowed, a value which cannot be changed. (default = .TRUE.)
- SNRMAX = upper limit for switching to straight NR search for stationary point location. (default = 0.10 or DPRED, whichever is smallest)
- OPTTOL = gradient convergence tolerance, in Hartree/Bohr. Used for optimizing to a stationary point. Convergence of a geometry search requires the rms gradient to be less than OPTTOL. (default=0.0001)
- HESS = selection of the initial hessian matrix, if STPT=.TRUE.
 = READ causes the hessian to be read from a \$HESS group.

= CALC causes the hessian to be computed. (Default)

- The rest of the parameters apply only to METHOD=SR

DELCOR = the corrector step should be smaller than this value before the next predictor step is taken. (default = 0.001)

MYSTEP = maximum number of micro iteration allowed to bring the corrector step length below DELCOR. (default=20)

SNUMH = stepsize used in the numerical differentiation of the Hessian to produce third derivatives. (default = 0.0001)

HSDFDB = flag to select determination of third derivatives. At the current geometry we need the gradient, the Hessian, and the partial third derivative matrix in the gradient direction.

If .TRUE., the gradient is calculated at the current geometry, and two Hessians are calculated at SNUMH distance to each side in the gradient direction. The Hessian at the geometry is formed as the average of the two displaced Hessians.

If .FALSE., both the gradient and Hessian are calculated at the current geometry, and one additional Hessian is calculated at SNUMH in the gradient direction.

The default double-sided differentiation produces a more accurate third derivative matrix, at the cost of an additional wave function and gradient. (default = .TRUE.)

See the 'further information' section for some help with GRADEXTR runs.

\$DRC group (relevant for RUNTYP=DRC)

This group governs the dynamical reaction coordinate, a classical trajectory method based on quantum chemical potential energy surfaces. In GAMESS these may be either ab initio or semi-empirical. Because the vibrational period of a normal mode with frequency 500 wavenumbers is 67 fs, a DRC needs to run for many steps in order to sample a representative portion of phase space. Almost all DRCs break molecular symmetry, so build your molecule with C1 symmetry in \$DATA, or specify NOSYM=1 in \$CONTRL. Restart data can be found in the job's OUTPUT file, with important results summarized to the IRCDATA file.

- NSTEP = The number of DRC points to be calculated, not including the initial point. (default = 1000)
- DELTAT = is the time step. (default = 0.1 fs)
- TOTIME = total duration of the DRC computed in a previous job, in fs. The default is the correct value when initiating a DRC. (default=0.0 fs)
-

In general, a DRC can be initiated anywhere, so \$DATA might contain coordinates of the equilibrium geometry, or a nearby transition state, or something else. You must also supply an initial kinetic energy, and the direction of the initial velocity, for which there are a number of options:

- EKIN = The initial kinetic energy (default = 0.0 kcal/mol) See also ENM, NVEL, and VIBLVL regarding alternate ways to specify the initial value.
- VEL = an array of velocity components, in Bohr/fs. When NVEL is false, this is simply the direction of the velocity vector. Its magnitude will be automatically adjusted to match the desired initial kinetic energy, and it will be projected so that the translation of the center of mass is removed. Give in the order vx1, vy1, vz1, vx2, vy2, ...
- NVEL = a flag to compute the initial kinetic energy from the input VEL using the sum of mass*VEL*VEL/2. This flag is usually selected only for restarts. (default=.FALSE.)
-

The next three allow the kinetic energy to be partitioned over all normal modes. The coordinates in \$DATA are likely to be from a stationary point! You must also supply a \$HESS group, which is the nuclear force constant matrix at the starting geometry..

- VIBLVL = a flag to turn this option on (default=.FALSE.)
- VIBENG = an array of energies (in units of multiples of the hv of each mode) to be imparted along each normal mode. The default is to assign the zeropoint energy only, VIBENG(1)=0.5, 0.5, ..., 0.5 when HESS=MIN, and 0.0, 0.5, ..., 0.5 if HESS=TS.. If given as a negative number, the initial direction of the velocity vector is along the reverse direction of the mode. "Reverse" means the phase of the normal mode is chosen such that the largest magnitude component is a negative value. An example might be

VIBENG(4)=2.5 to add two quanta to mode 4, along with zero point energy in all modes.

RCENG = reaction coordinate energy, in kcal/mol. This is the initial kinetic energy given to the imaginary frequency normal mode when HESS=TS. If this is given as a negative value, the direction of the velocity vector will be the "reverse direction", meaning the phase of the normal mode will be chosen so its largest component is negative.

The next two pertain to initiating the DRC along a single normal mode of vibration. No kinetic energy is assigned to the other modes. You must also supply a \$HESS group at the initial geometry.

NNM = The number of the normal mode to which the initial kinetic energy is given. The absolute value of NNM must be in the range 1, 2, ..., 3N-6. If NNM is a positive/negative value, the initial velocity will lie in the forward/reverse direction of the mode. "Forward" means the largest component of the normal mode is a positive value. (default=0)

ENM = the initial kinetic energy given to mode NNM, in units of vibrational quanta $h\nu$, so the amount depends on mode NNM's vibrational frequency, ν . If you prefer to impart an arbitrary initial kinetic energy to mode NNM, specify EKIN instead. (default = 0.0 quanta)

To summarize, there are 5 ways to initiate a trajectory:

1. VEL vector with NVEL=.TRUE. This is difficult to specify at your initial point, and so this option is mainly used when restarting your trajectory. The restart information is always in this format.
 2. VEL vector and EKIN with NVEL=.FALSE. This will give a desired amount of kinetic energy in the direction of the velocity vector.
 3. VIBLVL and VIBENG and possibly RCENG, to give some initial kinetic energy to all normal modes.
 4. NNM and ENM to give quanta to a single normal mode.
 5. NNM and EKIN to give arbitrary kinetic energy to a single normal mode.
-

The most common use of the next two is to analyze a trajectory with respect to the normal modes of a minimum energy geometry it travels around.

NMANAL = a flag to select mapping of the mass-weighted Cartesian DRC coordinates and velocity (conjugate momentum) in terms of normal modes at a nearby reference stationary point (which can be either a minimum or transition state). This reference geometry could in fact be the same as the initial point of the DRC, but does not need to be. If you choose this option, you must supply CO, HESS2, and a \$HESS2 group corresponding to the reference stationary point. (default=.FALSE.)

CO = an array of the coordinates of the stationary reference point (the coordinates in \$DATA might well be some other coordinates). Give in the

order x1,y1,z1,x2,y2,... in Angstroms.

The next options apply to input choices which may read a \$HESS at the initial DRC point, namely NNM or VIBLVL, or to those that read a \$HESS2 at some reference geometry (NMNAL).

HESS = MIN indicates the hessian supplied for the initial geometry corresponds to a minimum (default).
 = TS indicates the hessian is for a saddle point.
 HESS2 = MIN (default) or TS, the same meaning, for the reference geometry.

These are used to decide if modes 1-6 (minimum) or modes 2-7 (TS) are to be excluded from the hessian as the translational and rotational contaminants. If the initial and reference geometries are the same, these two Hessians will be duplicates of each other.

The next variables can cause termination of a run, if molecular fragments get too far apart or close together.

NFRGPR = Number of atom pairs whose distance will be checked. (default is 0)

IFRGPR = Array of the atom pairs. 2 times NFRGPR values.

FRGCUT = Array for a boundary distance (in Bohr) for atom pairs to end DRC calculations. The run will stop if any distance exceeds the tolerance, or if a value is given as a negative number, if the distance becomes shorter than the absolute value. In case the trajectory starts outside the bounds specified, they do not apply until after the trajectory reaches a point where the criteria are satisfied, and then goes outside again. Give NFRGPR values.

The final variables control the volume of output. Let F mean the first DRC point found in this run, and L mean the last DRC point of this run.

NPRTSM = summarize the DRC results every NPRTSM steps, to the file IRCDATA.
 (default = 1)

NPRT = 1 Print orbitals at all DRC points
 0 Print orbitals at F+L (default)
 -1 Never print orbitals

NPUN = 2 Punch all orbitals at all DRC points
 1 Punch all orbitals at F+L, and occupied orbitals at DRC points between
 points between
 0 Punch all orbitals at F+L only (default)
 -1 Never punch orbitals

References: see REFS.DOC.

\$GLOBOP group (optional, relevant to RUNTYP=GLOBOP)

This controls a search for the global minimum energy. It is primarily intended for locating the best position for effective fragment "solvent" molecules, perhaps with an ab initio "solute" present also. There are options for a single temperature Monte Carlo search, or a multi- temperature simulated annealing. Local minimization of some or all of the structures selected by the Monte Carlo is optional. The coordinates of accepted structures are written to file IRCDATA, unless MOVIE2 is chosen. See REFS.DOC for an overview of this RUNTYP.

- TEMPI = initial temperature used in the simulation. (default = 20000 K)
- TEMPF = final temperature. If TEMPF is not given and NTEMPS is greater than 1, TEMPF will be calculated based on a cooling factor of 0.95.
- NTEMPS = number of temperatures used in the simulation.
If NTEMPS is not given but TEMPF is given, NTEMP will be calculated based on a cooling factor of 0.95. If neither NTEMP nor TEMPF is given, the job defaults to a single temperature Monte Carlo calculation.
- NFRMOV = number of fragments to move on each step. (default=1)
- NGEOPT = number of geometries to be evaluated at each temperature.
(default = 100)
- NTRAN = number of translational steps in each block. (default=5)
- NROT = number of rotational steps in each block. (default=5)
- NBLOCK = the number of blocks of steps can be set directly with this variable, instead of being calculated from NGEOPT, NTRAN, and NROT, according to

$$\text{NBLOCK} = \text{NGEOPT} / (\text{NTRAN} + \text{NROT})$$
 If NBLOCK is input, the number of geometries at each temperature will be taken as

$$\text{NGEOPT} = \text{NBLOCK} * (\text{NTRAN} + \text{NROT})$$
 Each block has NTRAN translational steps followed by NROT rotational steps.
- MCMIN = flag to enable geometry optimization to minimize the energy is carried out every NSTMIN steps. (default=.true.)
- NSTMIN = After this number of geometry steps are taken, a local (Newton-Raphson) optimization will be carried out. If this variable is set to 1, a local minimization is carried out on every step, reducing the MC space to the set of local minima. Irrelevant if MCMIN is false. (Default=10)
- OPTN = if set to .TRUE., at the end of the run local minimizations are carried out on the final geometry and on the minimum-energy geometry.
(default=.FALSE.)
- SCALE = an array of length two. The first element is the initial maximum step size for the translational coordinates (Angstroms). The second element is the initial maximum stepsize for the rotational coordinates (pi-radians).

(defaults = 1,1)

- AIMOVE = step range for moving ab initio atoms in the MC simulation. If set to zero, the ab initio atoms do not move in MC. The motion of ab initio atoms is unsophisticated, as the move consists only of shifting each Cartesian coordinate in the range of plus AIMOVE to minus AIMOVE atomic units. Ab initio atoms are allowed to relax during possible geometry optimizations implied by MCMIN/NSTMIN. (default=0.0)
- ALPHA = controls the rate at which information from successful steps is folded into the maximum step sizes for each of the 6*(number of fragments) coordinates. ALPHA varies between 0 and 1. ALPHA=0 means do not change the maximum step sizes, and ALPHA=1 throws out the old step sizes whenever there is a successful step and uses the successful step sizes as the new maxima. This update scheme was used with the Parks method where all fragments are moved on every step. It is normally not used with the Metropolis method. (default = 0)
- DACRAT = the desired acceptance ratio, the program tries to achieve this by adjusting the maximum step size. (default = 0.5)
- UPDFAC = the factor used to update the maximum step size in the attempt to achieve the desired acceptance ratio (DACRAT). If the acceptance ratio at the previous temperature was below DACRAT, the step size is decreased by multiplying it by UPDFAC. If the acceptance ratio was above DACRAT, the step size is increased by dividing it by DACRAT. It should be between 0 and 1. (default = 0.95)
- SEPTOL = the separation tolerance between atoms in the ab initio piece and atoms in the fragments, as well as between atoms in different fragments. If a step moves atoms closer than this tolerance, the step is rejected. (default = 1.5 Angstroms)
- XMIN, XMAX, YMIN, YMAX, ZMIN, ZMAX = minimum and maximum values for the Cartesian coordinates of the fragment. If the first point in a fragment steps outside these boundaries, periodic boundary conditions are used and the fragment re-enters on the opposite side of the box. The defaults of -10 for minima and +10 for maxima should usually be changed.
- BOLTWT = method for calculating the Boltzmann factor, which is used as the probability of accepting a step that increases the energy.
 = STANDARD = use the standard Boltzmann factor, $\exp(-\Delta E/kT)$ (default)
 = AVESTEP = scale the temperature by the average step size, as recommended in the Parks reference when using values of ALPHA greater than 0.
- NPRT = controls the amount of output, with
 = -2 reduces output below that of -1
 = -1 reduces output further, needed for MCMIN=.true.
 = 0 gives minimal output (default)

= 1 gives the normal GAMESS amount of output

= 2 gives maximum output

For large simulations, even IOUT=0 may produce a log file too large to work with easily.

If geometry optimization is being done at each Monte Carlo generated structure, you can use the NPRT in \$STATPT to further suppress output.

RANDOM = controls the choice of random number generator.

= DEBUG uses a simple random number generator with a constant seed. Since the same sequence of random numbers is generated during each job, it is useful for debugging.

= RAND1 uses the simple random number generator used in DEBUG, but with a variable seed.

= RAND3 uses a more sophisticated random number generator described in Numerical Recipes, with a variable seed (default).

IFXFRG = array whose length is the number of fragments. It allows one or more fragments to be fixed during the simulation.

= 0 allows the fragment to move during the run

= 1 fixes the fragment

For example, IFXFRG(3)=1 would fix the third fragment, the default is IFXFRG(1)=0,0,0,...,0

MOVIE2 = a flag to create a series of structural data which can be shown as a movie by the Macintosh program Chem3D. The coordinates of each accepted geometry are written. The data is written to the file IRCDATA. (default=.FALSE.)

\$SURF group (relevant for RUNTYP=SURFACE)

This group allows you to probe a potential energy surface along a small grid of points. Note that there is no option to vary angles, only distances. The scan can be made for any SCFTYP, or for the MP2 or CI surface. You may specify two rather different calculations to be done at each point on the grid, through the RUNTYPn, SCFTYPn, and electron correlation keywords.

* * * below, 1 and 2 refer to different calculations * * *

RUNTP1,RUNTP2	= some RUNTYP supported in \$CONTRL First RUNTYP=RUNTP1 and then RUNTYP=RUNTP2 will be performed, for each point on the grid. The second run is omitted if RUNTP2 is set to NONE. default: RUNTP1=ENERGY RUNTP2=NONE
SCFTP1,SCFTP2	= some SCFTYP supported in \$CONTRL default: SCFTYP in \$CONTRL
CITYP1,CITYP2	= some CITYP supported in \$CONTRL default: CITYP in \$CONTRL
MPLEV1,MPLEV2	= some MPLEVL supported in \$CONTRL default: MPLEVL in \$CONTRL
CCTYP1,CCTYP2	= some CCTYP supported in \$CONTRL default: CCTYP in \$CONTRL
DFTYP1,DFTYP2	= some DFTTYP supported in \$DFT default: DFTTYP in \$DFT

You may need to help by giving values in \$CONTRL that will permit the program to estimate what is coming in the values here. For example, if you want to request Hessians here, it may be good to give RUNTYP=HESSIAN in \$CONTRL so that in its earliest stages of a job, the program can initialize for 2nd derivatives. There is less checking here than on \$CONTRL input, so don't request something impossible such as two correlation methods simultaneously, or analytic Hessians for MP2, or other things that are impossible.

* * * below, 1 and 2 refer to different coordinates * * *

IVEC1	= an array of two atoms, defining a coordinate from the first atom given to the second.
IGRP1	= an array specifying a group of atoms, which must include the second atom given in IVEC1. The entire group will be translated (rigidly) along the vector IVEC1, relative to the first atom given in IVEC1.
ORIG1	= starting value of the coordinate, which may be positive or negative. Zero corresponds to the distance given in \$DATA.
DISP1	= step size for the coordinate. If DISP1 is set to zero, then the keyword

GRID1 is read.

NDISP1 = number of steps to take for this coordinate.

GRID1 = an array of grid points at which to compute the energy. This option is an alternative to the ORIG1, DISP1 input which produces an equidistant grid. To use GRID1, one has to set DISP1=0.0. The number of grid points is in NDISP1, and is limited to at most 100 grid points. The input of GRID1(1)=ORIG1,ORIG1+DISP1,ORIG1+DISP1*2,... would reproduce an equidistant grid given by ORIG1 and DISP1.

ORIG1, DISP1, and GRID1 should be given in Angstrom. There are no reasonable defaults for these keywords.

IVEC2, IGRP2, ORIG2, DISP2, NDISP2, GRID2 have the same meaning as their "1" counterparts, and permit you to make counterparts, and permit you to make a two dimensional map along two displacement coordinates. If the "2" data are not input, the surface map proceeds in only one dimension.

\$LOCAL group (relevant for LOCAL=RUEDNBRG, BOYS, or POP)

This group allows input of additional data to control the localization methods. If no input is provided, the valence orbitals will be localized as much as possible, while still leaving the wavefunction invariant. There are many specialized options for Localized Charge Distribution analysis, and for EFP generation.

N.B. Since Boys localization needs the dipole integrals, do not turn off dipole moment calculation in \$ELMOM.

- MAXLOC = maximum number of localization cycles. This applies to BOYS or POP methods only. If the localization fails to converge, a different order of 2x2 pairwise rotations will be tried. (default=250)
- CVGLOC = convergence criterion. The default provides LMO coefficients accurate to 6 figures. (default=1.0E-6)
- SYMLOC = a flag to restrict localization so that orbitals of different symmetry types are not mixed. This option is not supported in all possible point groups. The purpose of this option is to give a better choice for the starting orbitals for GVB-PP or MCSCF runs, without destroying the orbital's symmetry. This option is compatible with each of the 3 methods of selecting the orbitals to be included. (default=.FALSE.)
- ORIENT = a flag to request orientation of the localized orbitals for bond-order analysis. After the localization, the orbitals on each atom are rotated only among themselves, in order to direct the orbitals towards neighboring atom's orbitals, to which they are bonded. The density matrix, or bond-order matrix, of these Oriented LMOs is readily interpreted as atomic populations and bond orders. This option can be used only for SCFTYP=MCSCF and LOCAL=RUEDENBRG. (default=.FALSE.)
- PRTLOC = a flag to control supplemental printout. The extra output is the rotation matrix to the localized orbitals, and, for the Boys method, the orbital centroids, for the Ruedenberg method, the coulomb and exchange matrices, for the population method, atomic populations. (default=.FALSE.)

The following keywords select the orbitals which are to be included in the localization. You may select from FCORE, NOUTA/NOUTB, or NINA/NINB, but may choose only one of these three groups.

- FCORE = flag to freeze all the chemical core orbitals present. All the valence orbitals will be localized. You must explicitly turn this option off to choose one of the other two orbital selection options. (default=.TRUE.)

NOUTA = number of alpha orbitals to hold fixed in the localization. (default=0)

MOOUTA = an array of NOUTA elements giving the numbers of the orbitals to hold fixed. For example, the input NOUTA=2 MOOUTA(1)=8,13 will freeze only orbitals 8 and 13. You must enter all the orbitals you want to

\$LOCAL

freeze, including any cores. This variable has nothing to do with cows.

NOUTB = number of beta orbitals to hold fixed in -UHF- localizations. (default=0)

MOOUTB = same as MOOUTA, except that it applies to the beta orbitals, in -UHF- wavefunctions only.

NINA = number of alpha orbitals which are to be included in the localization. (default=0)

MOINA = an array of NINA elements giving the numbers of the orbitals to be included in the localization. Any orbitals not mentioned will be frozen.

NINB = number of -UHF- beta MOs in the localization. (default=0)

MOINB = same as MOINA, except that it applies to the beta orbitals, in -UHF- wavefunctions only.

ORMFUL = this flag is relevant only to CISTEP=ORMAS MCSCF localizations. By default, the localization is restricted such that the multiple active spaces are not mixed, leaving the total wavefunction invariant. It may be used to localize within the full range of active MOs. (Default is .FALSE.)

- The following keywords are used for the localized charge distribution (LCD) energy decomposition.

EDCOMP = flag to turn on LCD energy decomposition. Note that this method is currently implemented for SCFTYP=RHF and ROHF and LOCAL=RUEDNBRG only. The SCF LCD forces all orbitals to be localized, overriding input on the previous page. See also LMOMP2 in the \$MP2 group. (default = .FALSE.)

MOIDON = flag to turn on LMO identification and subsequent LMO reordering, and assign nuclear LCD automatically. (default = .FALSE.)

DIPDCM = flag for LCD molecular dipole decomposition. (default = .FALSE.)

QADDCM = flag for LCD molecular quadrupole decomposition. (default = .FALSE.)

POLDPCM = flag to turn on LCD polarizability decomposition. This method is implemented for SCFTYP=RHF or ROHF and LOCAL=BOYS or RUEDNBRG. (default=.FALSE.)

POLNUM = flag to force numerical rather than analytical calculation of the polarizabilities. This may be useful in larger molecules. The numerical polarizabilities of bonds in or around aromatic rings sometimes are unphysical. (default=.FALSE.) See D.R.Garner, W.J.Stevens J.Phys.Chem. 93, 8263-8270 (1989).

POLAPP = flag to force calculation of the polarizabilities using a perturbation theory expression. This may be useful in larger molecules.

(default=.FALSE.) See R.M. Minikis, V. Kairys, J.H. Jensen
J.Phys.Chem.A 2000, submitted.

POLANG = flag to choose units of localized polarizability output. The default is Angstroms³, while false will give Bohr³. (default=.TRUE.)

ZDO = flag for LCD analysis of a composite wave function, given in a \$VEC group of a van der Waals complex, within the zero differential overlap approximation. The MOs are not orthonormalized and the intermolecular electron exchange energy is neglected. In addition, the molecular overlap matrix is printed out. This is a very specialized option.
(default = .FALSE.)

- The following keywords can be used to define the nuclear part of an LCD. They are usually used to rectify mistakes in the automatic definition made when MOIDON=.TRUE. The index defining the LMO number then refers to the reordered list of LMOs.

NMOIJ = array giving the number of nuclei assigned to a particular LMO.

IJMO = is an array of pairs of indices (I,J), giving the row (nucleus I) and column (orbital J) index of the entries in ZIJ and MOIJ.

MOIJ = arrays of integers K, assigning nucleus K as the site of the Ith charge of LCD J.

ZIJ = array of floating point numbers assigning a charge to the Ith charge of LCD J.

IPROT = array of integers K, defining nucleus K as a proton.

DEPRNT = a flag for additional decomposition printing, such as pair contributions to various energy terms, and centroids of the Ruedenberg orbitals.
(default = .FALSE.)

- The following keywords are used to build large EFPs from several RUNTYP=MAKEFP runs on smaller molecular fragments, by excluding common regions of overlap. For example, an EFP for n-octanol can be build from two MAKEFP runs, on n-pentane and n-pentanol,

CH3CH2CH2CH2-CH2CH2CH2CH2OH
CH3CH2CH2CH2[-CH3]
[CH3]-CH2CH2CH2CH2OH

by excluding overlapping regions shown in brackets from the two EFPs. See J.Phys.Chem.A 105, 3829-3837, (2001) for more information.

NOPATM = array of atoms that define an area to be excluded from a DMA (\$STONE) during a RUNTYP=MAKEFP run. All atomic centers specified, and the midpoints of any bonds to them, are excluded as expansion points. The density due to all LMOs primarily centered on these atoms are excluded from the DMA (see also KMIDPT). Furthermore, polarizability tensors for these LMOs are excluded.

\$LOCAL, \$TWOEI

- KPOINT = array of "boundary atoms", those atoms that are covalently bonded to the atoms given in NOATM.
- KMIDPT = flag to indicate whether the density due to bond LMOs (and associated expansion points) between the NOPATM atoms and the KPOINT atoms are to be included in the DMA. (default = .TRUE.)
- NODENS = an array that specifies the atoms for which the associated electronic density will be removed before the multipole expansion. This provides an EFP with net integer charge.
(P.A.Molina, H.Li, J.H.Jensen J.Phys.Chem.B mss in prep, 2003).
-

For hints about localizations, and the LCD energy decomposition, see the 'further information' section.

\$TWOEI group (relevant for EDCOMP=.TRUE. in \$LOCAL)

Formatted transformed two-electron Coulomb and Exchange integrals as punched during a LOCAL=RUEDNBRG run. If this group is present it will automatically be read in during such a run and the two-electron integrals do not have to be re-transformed. This group is especially useful for EDCOMP=.TRUE. runs when the localization has to be repeated for different definitions of nuclear LCDs.

\$TRUNCN group (optional, relevant for RHF)

This group controls the truncation of some of the localized orbitals to just the AOs on a subset of the atoms. This option is particularly useful to generate localized orbitals to be frozen when the effective fragment potential is used to partition a system across a chemical bond. In other words, this group prepares the frozen buffer zone orbitals. This group should be used in conjunction with RUNTYP=ENERGY (or PROP if the orbitals are available) and either LOCAL=RUEDNBRG or BOYS, with MOIDON set in \$LOCAL.

- DOPROJ = flag to activate MO projection/truncation, the default is to skip this (default=.FALSE.)

- AUTOID = forces identification of MOs (analogous to MOIDON in \$LOCAL). This keyword is provided in case the localized orbitals are already present in \$VEC, in which case this is a faster RUNTYP=PROP with LOCAL=NONE job. Obviously, GUESS=MOREAD. (default=.FALSE.)

- PLAIN = flag to control the MO tail truncation. A value of .FALSE. uses corresponding orbital projections, H.F.King, R.E.Stanton, H.Kim, R.E.Wyatt, R.G.Parr J. Chem. Phys. 47, 1936-1941(1967) and generates orthogonal orbitals. A value of .TRUE. just sets the unwanted AOs to zero, so the resulting Mos need to go through the automatic orthogonalization step when MOREAD in the next job. (default=.FALSE.)

- IMOPR = an array specifying which MOs to be truncated. In most cases involving normal bonding, the options MOIDON or AUTOID will correctly identify all localized MOs belonging to the atoms in the zone being truncated. However, you can inspect the output, and give a list of all MOs which you want to be truncated in this array, in case you feel the automatic assignment is incorrect. Any orbital not in the truncation set, whether this is chosen automatically or by IMOPR, is left completely unaltered.

There are now two ways to specify what orbitals are to be truncated. The most common usage is for preparation of a buffer zone for QM/MM computations, with an Effective Fragment Potential representing the non-quantum part of the system. This input is NATAB, NATBF, ICAPFR, ICAPBF, in which case the \$DATA input must be sorted into three zones. The first group of atoms are meant to be treated in later runs by full quantum mechanics, the second group by frozen localized orbitals as a 'buffer', and the third group is to be substituted later by an effective fragment potential (multipoles, polarizabilities, ...). Note that in the DOPROJ=.TRUE. run, all atoms are still quantum atoms.

- NATAB = number of atoms to be in the 'ab initio' zone.

- NATBF = number of atoms to be in the 'buffer' zone. The program can obtain the number of atoms in the remaining zone by subtraction, so it need not be input.

In case the MOIDON or AUTOID options lead to confused assignments (unlikely in ordinary bonding situations around the buffer zone), there are two fine tuning values.

\$TRUNCN

ICAPFR = array indicating the identity of "capping atoms" which are on the border between the ab initio and buffer zones (in the ab initio zone).

ICAPBK = array indicating the identity of "capping atoms" which are on the border between the buffer and EFP zones (in the effective fragment zone).

See also IXCORL and IXLONE below.

In case truncation seems useful for some other purpose, you can specify the atoms in any order within the \$DATA group, by the IZAT/ILAT approach. You are supposed to give only one of these two lists, probably whichever is shorter:

IZAT = an array containing the atoms which are NOT in the buffer zone.

ILAT = an array containing the atoms which are in the buffer zone.

The AO coefficients of the localized orbitals present in the buffer zone which lie on atoms outside the buffer will be truncated.

See also IXCORL and IXLONE below.

The next two values let you remove additional orbitals within the buffer zone from the truncation process, if that is desirable. These arrays can only include atoms that are already in the buffer zone, whether this was defined by NATBF, or IZAT/ILAT. The default is to include all core and lone pair orbitals, not just bonding orbitals, as the buffer zone orbitals.

IXCORL = an array of atoms whose core and lone pair orbitals are to be considered as not belonging to the buffer zone orbitals.

IXLONE = an array of atoms for which only the lone pair orbitals are to be considered as not belonging to the buffer zone orbitals.

The final option controls output of the truncated orbitals to file PUNCH for use in later runs:

NPUNOP	=	punch out option for the truncated orbitals
	= 1	the MOs are not reordered.
	= 2	punch the truncated MOs as the first vectors in the \$VEC MO set, with untransformed vectors following immediately after. (default)

\$ELMOM group (not required)

This group controls electrostatic moments calculation.

This group controls electrostatic moments calculation. The symmetry properties of multipoles are discussed in

A.Gelessus, W.Thiel, W.Weber
J.Chem.Ed. 72, 505-508(1995)

IEMOM	=	0	skip this property
		1	calculate monopole and dipole (default)
		2	also calculate quadrupole moments
		3	also calculate octopole moments
WHERE	=	COMASS	center of mass (default)
		NUCLEI	at each nucleus
		POINTS	at points given in \$POINTS.
OUTPUT	=	PUNCH, PAPER, or BOTH (default)	
IEMINT	=	0	skip printing of integrals (default)
		1	print dipole integrals
		2	also print quadrupole integrals
		3	also print octopole integrals
		-2	print quadrupole integrals only
		-3	print octopole integrals only

The quadrupole and octopole tensors on the printout are formed according to the definition of Buckingham. Caution: only the first nonvanishing term in the multipole charge expansion is independent of the coordinate origin chosen, which is normally the center of mass.

\$ELPOT group (not required)

This group controls electrostatic potential calculation.

IEPOT	=	0	skip this property (default)
		1	calculate electric potential
WHERE	=	COMASS	center of mass
		NUCLEI	at each nucleus (default)
		POINTS	at points given in \$POINTS
		GRID	at grid given in \$GRID
		PDC	at points controlled by \$PDC.
OUTPUT	=	PUNCH, PAPER, or BOTH (default)	

This property is the electrostatic potential $V(a)$ felt by a test positive charge, due to the molecular charge density. A nucleus at the evaluation point is ignored. If this property is evaluated at the nuclei, it obeys the equation

$$\sum_{\text{nuclei } a} Z(a) \cdot V(a) = 2 \cdot V(\text{nn}) + V(\text{ne}).$$

The electronic portion of this property is called the diamagnetic shielding.

\$ELDENS group (not required)

This group controls electron density calculation.

IEDEN	= 0	skip this property (default)
	= 1	compute the electron density.
MORB	=	The molecular orbital whose electron density is to be computed. If zero, the total density is computed. (default=0)
WHERE	= COMASS	center of mass
	NUCLEI	at each nucleus (default)
	POINTS	at points given in \$POINTS
	GRID	at grid given in \$GRID
OUTPUT	=	PUNCH, PAPER, or BOTH (default)
IEDINT	= 0	skip printing of integrals (default)
	1	print the electron density integrals

\$ELFLDG group (not required)

This group controls electrostatic field and electric field gradient calculation.

IEFLD	= 0	skip this property (default)
	1	calculate field
	2	calculate field and gradient
WHERE	= COMASS	center of mass
	NUCLEI	at each nucleus (default)
	POINTS	at points given in \$POINTS
OUTPUT	=	PUNCH, PAPER, or BOTH (default)
IEFINT	= 0	skip printing these integrals (default)
	1	print electric field integrals
	2	also print field gradient integrals
	-2	print field gradient integrals only

The Hellman-Feynman force on a nucleus is the nuclear charge multiplied by the electric field at that nucleus. The electric field is the gradient of the electric potential, and the field gradient is the hessian of the electric potential. The components of the electric field gradient tensor are formed in the conventional way, i.e. see D.Neumann and J.W.Moskowitz.

\$POINTS, \$GRID, \$PDC**\$POINTS group (not required)**

This group is used to input points at which properties will be computed. This first card in the group must contain the string ANGS or BOHR, followed by an integer NPOINT, the number of points to be used. The next NPOINT cards are read in free format, containing the X, Y, and Z coordinates of each desired point.

\$GRID group (not required)

This group is used to input a grid (plane through the molecule) on which properties will be calculated.

ORIGIN(i) = coordinates of the lower left corner of the plot.
 XVEC(i) = coordinates of the lower right corner of the plot.
 YVEC(i) = coordinates of the upper left corner of the plot.
 SIZE = grid increment, default is 0.25.
 UNITS = units of the above four values, it can be either BOHR or ANGS (the default).

Note that XVEC and YVEC are not necessarily parallel to the X and Y axes, rather they are the axes which you desire to see plotted by the MEPMAP contouring program.

For conversion factors, and references see the 'further information' section.

\$PDC group (relevant if WHERE=PDC in \$ELPOT)

This group determines the points at which to compute the electrostatic potential, for the purpose of fitting atomic charges to this potential. Constraints on the fit which determines these "potential determined charges" can include the conservation of charge, the dipole, and the quadrupole.

PTSEL = determines the points to be used, choose from
 GEODESIC to use a set of points on several fused sphere van der Waals surfaces, with points selected using an algorithm due to Mark Spackman. The results are similar to those from the Kollman/Singh method, but are less rotation dependent. (default)
 CONNOLLY to use a set of points on several fused sphere van der Waals surfaces, with points selected using an algorithm due to Michael Connolly. This is identical to the method used by Kollman & Singh (see below)

	CHELPG	to use a modified version of the CHELPG algorithm, which produces a symmetric grid of points for a symmetric molecule.
CONSTR	= NONE	no fit is performed. The potential at the points is instead output according to OUTPUT in \$ELPOT.
	CHARGE	the sum of fitted atomic charges is constrained to reproduce the total molecular charge. (default)
	DIPOLE	fitted charges are constrained to exactly reproduce the total charge and dipole.
	QUPOLE	fitted charges are constrained to exactly reproduce the charge, dipole, and quadrupole.

Note: the number of constraints cannot exceed the number of parameters, which is the number of nuclei. Planar molecules afford fewer constraint equations, namely two dipole constraints and three quadrupole constraints, instead of three and five, respectively.

* * * the next 5 pertain to PTSEL=GEODESIC or CONNOLLY * * *

VDWSCL	=	scale factor for the first shell of VDW spheres. The default of 1.4 seems to be an empirical best value. Values for VDW radii for most elements up to Z=36 are internally stored.
VDWINC	=	increment for successive shells (default = 0.2). The defaults for VDWSCL and VDWINC will result in points chosen on layers at 1.4, 1.6, 1.8 etc times the VDW radii of the atoms.
LAYER	=	number of layers of points chosen on successive fused sphere VDW surfaces (default = 4)
NFREQ	=	flag for particular geodesic tessellation of points. Only relevant if PTSEL=GEODESIC. Options are: (10*h + k) for {3,5+}h,k tessellations -(10*h + k) for {5+,3}h,k tessellations (of course both nh and nk must be less than 10, so NFREQ must lie within the range -99 to 99) The default value is NFREQ=30 (=03)
PTDENS	=	density of points on the surface of each scaled VDW sphere (in points per square au). Only relevant if PTSEL=CONNOLLY. Default is 0.28 per au squared, which corresponds to 1.0 per square Angstrom, the default recommended by Kollman & Singh.

* * * the next two pertain to PTSEL=CHELPG * * *

RMAX	=	maximum distance from any point to the closest atom. (default=3.0 Angstroms)
DELR	=	distance between points on the grid. (default=0.8 Angstroms)

- MAXPDC = an estimate of the total number of points whose electrostatic potential will be included in the fit. (default=10000)
-
- CENTER = an array of coordinates at which the moments were computed.
- DPOLE = the molecular dipole.
- QPOLE = the molecular quadrupole.
- PDUNIT = units for the above values. ANG (default) will mean that the coordinates are in Angstroms, the dipole in Debye, and quadrupole in Buckingham. BOHR implies atomic units for all 3.

Note: it is easier to compute the moments in the current run, by setting IEMOM to at least 2 in \$ELMOM. However, you could fit experimental data, for example, by reading it in here.

There is no unique way to define fitted atomic charges. Smaller numbers of points at which the electro-static potential is fit, changes in VDW radii, asymmetric point location, etc. all affect the results. A useful bibliography is

U.C.Singh, P.A.Kollman, J.Comput.Chem. 5, 129-145(1984)
 L.E.Chirlain, M.M.Francl, J.Comput.Chem. 8, 894-905(1987)
 R.J.Woods, M.Khalil, W.Pell, S.H.Moffatt, V.H.Smith, J.Comput.Chem. 11, 297-310(1990)
 C.M.Breneman, K.B.Wiberg, J.Comput.Chem. 11, 361-373(1990)
 K.M.Merz, J.Comput.Chem. 13, 749(1992)
 M.A.Spackman, J.Comput.Chem. 17, 1-18(1996)

\$MOLGRF group (relevant only if you have MOLGRAPH)

This option provides an interface for viewing orbitals through a commercial package named MOLGRAPH, from Daikin Industries. Note that this option uses three disk files which are not defined in the GAMESS execution scripts we provide, since we don't use MOLGRAPH ourselves. You will need to define files 28, 29, 30, as generic names PRGRID, COGRID, MOGRID, of which the latter is passed to MOLGRAPH.

- GRID3D = a flag to generate 3D grid data. (default is .false.).
- TOTAL = a flag to generate a total density grid data. "Total" means the sum of the orbital densities given by NPLT array. (default is .false.).
- MESH = numbers of grids. You can use different numbers for three axes. (default is MESH(1)=21,21,21).
- BOUND = boundary coordinates of a 3D graphical cell. The default is that the cell is larger than the molecular skeleton by 3 bohr in all directions. E.g.,

BOUND(1)=xmin,xmax,ymin,ymax,zmin,zmax

NPLOTS = number of orbitals to be used to generate 3D grid data. (default is NPLOTS=1).

NPLT = orbital IDs. The default is 1 orbital only, the HOMO or SOMO. If the LOCAL option is given in \$CONTRL, localized orbital IDs should be given. For example, NPLT(1)=n1,n2,n3,...

CHECK = debug option, printing some of the grid data.

If you are interested in graphics, look at the WWW page for information about other graphics packages with GAMESS.

\$STONE group (optional)

This group defines the expansion points for Stone's distributed multipole analysis (DMA) of the electrostatic potential.

The DMA takes the multipolar expansion of each overlap charge density defined by two gaussian primitives, and translates it from the center of charge of the overlap density to the nearest expansion point. Some references for the method are

Stone, Chem.Phys.Lett. 83, 233 (1981)
 Price and Stone, Chem.Phys.Lett. 98, 419 (1983)
 Buckingham and Fowler, J.Chem.Phys. 79, 6426 (1983)
 Stone and Alderton, Mol.Phys. 56, 1047 (1985)

The existence of a \$STONE group in the input is what triggers the analysis. Enter as many lines as you wish, in any order, terminated by a \$END record.

ATOM i name, where

ATOM	is a keyword indicating that a particular atom is selected as an expansion center.
i	is the number of the atom
name	is an optional name for the atom. If not entered the name will be set to the name used in the \$DATA input.

ATOMS is a keyword selecting all nuclei in the molecule as expansion points. No other input on the line is necessary.

BONDS is a keyword selecting all bond midpoints in the molecule as expansion points. No other input on the line is necessary.

\$STONE

BOND i j name, where

BOND	is a keyword indicating that a bond mid-point is selected as an expansion center.
i,j	are the indices of the atoms defining the bond, corresponding to two atoms in \$DATA.
name	an optional name for the bond midpoint. If omitted, it is set to 'BOND'.

CMASS is a keyword selecting the center of mass as an expansion point. No other input on the line is necessary.

POINT x y z name, where

POINT	is a keyword indicating that an arbitrary point is selected as an expansion point.
x,y,z	are the coordinates of the point, in Bohr.
name	is an optional name for the expansion point. If omitted, it is set to 'POINT'.

While making the EFPs for QM/MM run, a single keyword QMMMBUF is necessary. Adding additional keywords may lead to meaningless results. The program will automatically select atoms and bond midpoints which are outside the buffer zone as the multipole expansion points.

QMMMBUF nmo, where

QMMMBUF	is a keyword specifying the number of QM/MM buffer molecular orbitals, which must be the first NMO orbitals in the MO set. These orbitals must be frozen in the buffer zone, so this is useful only if \$MOFRZ is given.
NMO	is the number of buffer MO-s (if NMO is omitted, it will be set to the number of frozen MOs in \$MOFRZ)

The second and third moments on the printout can be converted to Buckingham's tensors by formula 9 of A.D.Buckingham, Quart.Rev. 13, 183-214 (1959)
 These can in turn be converted to spherical tensors by the formulae in the appendix of S.L.Price, et al. Mol.Phys. 52, 987-1001 (1984)

\$RAMAN group (relevant for all SCFTYPs)

This input controls the computation of Raman intensity by the numerical differentiation procedure of Komornicki and others. It is applicable to any wavefunction for which the analytic gradient is available, including some MP2 and CI cases. The calculation involves the computation of 19 nuclear gradients, one without applied electric fields, plus 18 no symmetry runs with electric fields applied in various directions. The numerical second differencing produces intensity values with 2-3 digits of accuracy.

This run must follow an earlier RUNTYP=HESSIAN job, and the \$GRAD and \$HESS groups from that first job must be given as input. If the \$DIPDR is computed analytically by this Hessian job, it too may be read in, if not, the numerical Raman job will evaluate \$DIPDR. Once the data from the 19 applied fields is available, the \$ALPDR tensor is evaluated. Then the nuclear derivatives of the dipole moment and alpha polarizability will be combined with the normal coordinate information to produce the IR and Raman intensity of each mode.

To study isotopic substitution speedily, input the \$GRAD, \$HESS, \$DIPDR, and \$ALPDR groups along with the desired atomic masses in \$MASS.

The code does not permit any semi-empirical or solvation models to be used.

EFIELD = applied electric field strength. The literature suggests values in the range 0.001 to 0.005. (default = 0.002 a.u.)

=====

\$ALPDR group (relevant for RUNTYP=HESSIAN or RAMAN)

Formatted alpha derivative tensor, punched by a previous RUNTYP=RAMAN job. If both \$DIPDR and this group are found in the input file, the applied field computation will be skipped, to immediately evaluate IR and Raman intensities.

If this group is found during a Hessian job, the Raman intensities will be added to the output. You might want to run as RUNTYP=HESSIAN instead of RUNTYP=RAMAN in order to have access to PROCT or the other options available in the \$FORCE group.

\$MOROKM group (relevant for RUNTYP=MOROKUMA)

This group controls how the supermolecule input in the \$DATA group is divided into two or more monomers. Both the supermolecule and its constituent monomers must be well described by RHF wavefunctions.

- MOROKM = a flag to request Morokuma-Kitaura decomposition. (default is .TRUE.)
- RVS = a flag to request "reduced variation space" decomposition. This differs from the Morokuma option, and one or the other or both may be requested in the same run. (default is .FALSE.)
- BSSE = a flag to request basis set superposition error be computed. You must ensure that CTPSPL is selected. This option applies only to MOROKM decompositions, as a basis superposition error is automatically generated by the RVS scheme. This is not the full Boys counterpoise correction, as explained in the reference. (default is .FALSE.)
-
- IATM = An array giving the number of atoms in each of the monomer. Up to ten monomers may be defined. Your input in \$DATA must have all the atoms in the first monomer defined before the atoms in the second monomer, before the third monomer... The number of atoms belonging to the final monomer can be omitted. There is no sensible default for IATM, so don't omit it from your input.
- ICHM = An array giving the charges of the each monomer. The charge of the final monomer may be omitted, as it is fixed by ICH in \$CONTRL, which is the total charge of the supermolecule. The default is neutral monomers, ICHM(1)=0,0,0,...
- EQU = a flag to indicate all monomers are equivalent by symmetry (in addition to containing identical atoms). If so, which is not often true, then only the unique computations will be done. (default is .FALSE.)
- CTPSPL = a flag to decompose the interaction energy into charge transfer plus polarization terms. This is most appropriate for weakly interacting monomers. (default is .TRUE.)
- CTPLX = a flag to combine the CT and POL terms into a single term. If you select this, you might want to turn CTPSPL off to avoid the extra work that decomposition entails, or you can analyze both ways in the same run (default=.FALSE.)
- RDENG = a flag to enable restarting, by reading the lines containing "FINAL ENERGY" from a previous run. The \$ENERGY group is single lines read under format A16,F20.10 containing the E, and a card \$END to complete. The 16 chars = anything. (default is .FALSE.)
-

The present implementation has some quirks:

1. The initial guess of the monomer orbitals is not controlled by \$GUESS. The program first looks for a \$VEC1, \$VEC2, ... group for each monomer. If they are found, they will be MOREAD. If any of these are missing, the guess for that monomer will be constructed by HCORE. Check your monomer energies carefully! The initial guess orbitals for the supermolecule are formed by a block diagonal matrix of the monomer orbitals.
2. The use of symmetry is turned off internally.
3. There is no direct SCF option. File ORDINT will be a full C1 list of integrals. File AOINTS will contain whatever subset of these is needed for each particular decomposition step. So extra disk space is needed compared to RUNTYP=ENERGY.
4. This kind of run applies only to ab initio cases.
5. This kind of run will work in parallel.
6. Spherical harmonics may not be used.

References :

C.Coulson in "Hydrogen Bonding", D.Hadzi, H.W.Thompson, Eds., Pergamon Press, NY, 1957 , pp 339-360.

C.Coulson Research, 10, 149-159 (1957).

K.Morokuma J.Chem.Phys. 55, 1236-44 (1971).

K.Kitaura, K.Morokuma Int.J.Quantum Chem. 10, 325 (1976).

K.Morokuma, K.Kitaura in "Chemical Applications of Electrostatic Potentials", P.Politzer,D.G.Truhlar, Eds. Plenum Press, NY, 1981 , pp 215-242.

The method coded is the newer version described in the latter two papers.

Note that the CT term is computed separately for each monomer, as described in the words below equation 16 of the 1981 paper, not simultaneously.

Reduced Variational Space:

W.J.Stevens, W.H.Fink, Chem.Phys.Lett. 139, 15-22(1987).

A comparison of the RVS and Morokuma decompositions can be found in the review article: "Wavefunctions and Chemical Bonding" M.S.Gordon, J.H.Jensen in "Encyclopedia of Computational Chemistry", volume 5, P.V.R.Schleyer, editor, John Wiley and Sons, Chichester, 1998 .

BSSE during Morokuma decomposition:

R.Cammi, R.Bonaccorsi, J.Tomasi Theoret.Chim.Acta 68, 271-283(1985).

The present implementation:

"Energy decomposition analysis for many-body interactions, and application to water complexes" W.Chen, M.S.Gordon J.Phys.Chem. 100, 14316-14328(1996)

\$FFCALC group (relevant for RUNTYP=FFIELD)

This group permits the study of the influence of an applied electric field on the wavefunction. The most common finite field calculation applies a sequence of fields to extract the linear polarizability and first and second order hyperpolarizability. The method is general, and so works for all ab initio wavefunctions in GAMESS.

EFIELD = applied electric field strength (default=0.001 a.u.)

IAXIS and JAXIS specify the orientation of the applied field. 1,2,3 mean x,y,z respectively. The default is IAXIS=3 and JAXIS=0.

If IAXIS=i and JAXIS=0, the program computes alpha(ii), beta(iii), and gamma(iiii) from the energy changes, and a few more components from the dipole changes. Five wavefunction evaluations are performed.

If IAXIS=i and JAXIS=j, the program computes the cross terms beta(ijj), beta(iij), and gamma(iijj) from the energy changes, and a few more components from the dipole changes. This requires nine evaluations of the wavefunction.

AOFF = a flag to permit evaluation of alpha(ij) when the dipole moment is not available. This is necessary only for MP2, and means the off-axial calculation will do 13, not 9 energy evaluations. Default=.FALSE.

SYM = a flag to specify when the fields to be applied along the IAXIS and/or JAXIS (or according to EONE below) do not break the molecular symmetry. Since most fields do break symmetry, the default is .FALSE.

ONEFLD = a flag to specify a single applied field calculation will be performed. Only the energy and dipole moment under this field are computed. If this option is selected, only SYM and EONE input is heeded. The default is .FALSE.

EONE = an array of the three x,y,z components of the single applied field.

Notes on RUNTYP=FFIELD.

Finite field calculations require large basis sets, and extraordinary accuracy in the wavefunction. To converge the SCF to many digits is sometimes problematic, but we suggest you use the input to increase integral accuracy and wavefunction convergence, for example

```
$CONTRL ICUT=20 ITOL=30 INTTYP=HONDO $END
$SCF     CONV=1.0d-10 FDIFF=.FALSE. $END
```

In many cases, the applied fields will destroy the molecular symmetry. This means the integrals are calculated once with point group symmetry to do the initial field free wavefunction evaluation, and then again with point group symmetry turned off. If the fields applied do not destroy symmetry, you can avoid this second calculation of the integrals by SYM=.TRUE. This option also permits use of symmetry during the applied field wavefunction evaluations.

Examples of fields that do not break symmetry are a Z-axis field for an axial point group which is not centrosymmetric (i.e. C_{2v}). However, a second field in the X or Y direction does break the C_{2v} symmetry. Application of a Z-axis field for benzene breaks D_{6h} symmetry. However, you could enter the group as C_{6v} in \$DATA while using D_{6h} coordinates, and regain the prospect of using SYM=.TRUE. If you wanted to go on to apply a second field for benzene in the X direction, you might want to enter C_s in \$DATA, which will necessitate the input of two more carbon and hydrogen atom, but recovers use of SYM=.TRUE.

Reference: H.A.Kurtz, J.J.P.Stewart, K.M.Dieter J.Comput.Chem. 11, 82-87 (1990).

For analytic computation of static and also frequency dependent NLO properties, for closed shell cases, see the \$TDHF group.

\$TDHF group (relevant for SCFTYP=RHF if RUNTYP=TDHF)

This group permits the analytic calculation of various static and/or frequency dependent polarizabilities, with an emphasis on important NLO properties such as second and third harmonic generation. The method is programmed only for closed shell wavefunctions, at the semi-empirical or ab initio level. Ab initio calculations may be direct SCF, or parallel, if desired.

Because the Fock matrices computed during the time-dependent Hartree-Fock CPHF are not symmetric, you may not use symmetry. You must enter NOSYM=1 in \$CONTRL!

For a more general numerical approach to the static properties, see \$FFCALC.

NFREQ = Number of frequencies to be used. (default=1)

FREQ = An array of energy values in atomic units. For example: if NFREQ=3 then FREQ(1)=0.0,0.1,0.25. By default, only the static polarizabilities are computed. (default is freq(1)=0.0)

The conversion factor from Hartree to wave numbers is 219,474.6, and the wavelength is given (in nm) by 45.56/FREQ.

MAXITA = Maximum number of iterations for an alpha computation. (default=100)

MAXITU = Maximum number of iterations in the second order correction calculation. This applies to iterative beta values and all gammas. (default=100)

ATOL = Tolerance for convergence of first-order results. (default=1.0d-05)

BTOL = Tolerance for convergence of second-order results. (default=1.0d-05)

RETDHF = a flag to choose starting points for iterative calculations from best previous results. (default=.true.)

* * * the following NLO properties are available * * *

INIB	=	0 turns off all beta computation (default)
	=	1 calculates only noniterative beta
	=	2 calculate iterative and noniterative beta
		The next flags allow further BETA tuning
BSHG	=	Calculate beta for second harmonic generation.
BEOPE	=	Calculate beta for electrooptic Pockels effect.
BOR	=	Calculate beta for optical rectification.
INIG	=	0 turns off all gamma computation (default)
	=	1 calculates only noniterative gamma
	=	2 calculate iterative and noniterative gamma
		The next flags allow further GAMMA tuning
GTHG	=	Calculate gamma for third harmonic generation.
GEFISH	=	Calculate gamma for electric-field induced second harmonic generation.
GIDRI	=	Calculate gamma for intensity dependent refractive index.
GOKE	=	Calculate gamma for optical Kerr effect.

These will be computed only if a nonzero energy is requested. The default for each flag is .TRUE., and they may be turned off individually by setting some .FALSE. Note however that the program determines the best way to calculate them. For example, if you wish to have the SHG results but no gamma results are needed, the SHG beta will be computed in a non-iterative way from $\alpha(w)$ and $\alpha(2w)$. However if you request the computation of the THG gamma, the second order $U(w,w)$ results are needed and an iterative SHG calculation will be performed whether you request it or not, as it is a required intermediate.

Reference: S.P.Karna, M.Dupuis J.Comput.Chem. 12, 487-504 (1991).
P.Korambath, H.A.Kurtz, in "Nonlinear Optical Materials", ACS Symposium Series 628,
S.P.Karna and A.T.Yeates, Eds. pp 133-144, Washington DC, 1996 .
Review: D.P.Shelton, J.E.Rice, Chem.Rev. 94, 3-29(1994).

\$EFRAG group (optional)

This group gives the name and position of one or more effective fragment potentials. It consists of a series of free format card images, which may not be combined onto a single line! The position of a fragment is defined by giving any three points within the fragment, relative to the ab initio system defined in \$DATA, since the effective fragments have a frozen internal geometry. All other atoms within the fragment are defined by information in the \$FRAGNAME group.

-1- a line containing one or more of these options:

COORD	=	CART	selects use of Cartesians coords to define the fragment position at line -3-. (default)
	=	INT	selects use of Z-matrix internal coordinates at line -3-.
POLMETHD=	SCF		indicates the induced dipole for each fragment due to the ab initio electric field and other fragment fields is updated only once during each SCF iteration.
	=	FRGSCF	requests microiterations during each SCF iteration to make induced dipoles due to ab initio and other fragment fields self consistent among the fragments. (Default)

Both methods converge to the same dipolar interaction.

POSITION	=	OPTIMIZE	Allows full optimization within the ab initio part, and optimization of the rotational and translational motions of each fragment. (default)
	=	FIXED	Allows full optimization of the ab initio system, but freezes the position of the fragments. This makes sense only with two or more fragments, as what is frozen is the fragments' relative orientation.
	=	EFOPT	the same as OPTIMIZE, but if the fragment gradient is large, up to 5 geometry steps in which only the fragments move may occur, before the geometry of the ab initio piece is relaxed. This may save time by reusing the two electron integrals for the ab initio system.

NBUFFMO	=	n	First n orbitals in the MO matrix are deemed to belong to the QM/MM buffer and will be excluded from the interaction with the EFP region. This makes sense only if these first MOs are frozen via the \$MOFRZ group.
---------	---	---	--

Note that other parameters in the developing EFP-2 model are not documented in the \$FRAGNAME documentation below.

MXBF	=	n	maximum number of basis functions in the EFP-2 potential
MXMO	=	n	maximum number of MOs in the EFP-2 potential.

Input a blank line if all the defaults are acceptable.

-2- FRAGNAME=XXX

XXX is the name of the fragment whose coordinates are to be given next. All other information defining the fragment is given in a supplemental \$XXX group, which is referred to below as a \$FRAGNAME group.

Two different water potentials are internally stored. FRAGNAME=H2OEF2 will select a water potential developed at the RHF/DZP level, while FRAGNAME=H2ODFT will select a potential corresponding to B3LYP/DZP (see \$BASIS for the precise meaning of DZP). If you choose one of these internally stored potentials, you do not need to input either a \$FRAGNAME or \$FRGPOL groups.

-3- NAME, X, Y, Z (COORD=CART)
 NAME, I, DISTANCE, J, BEND, K, TORSION (COORD=INT)

NAME = the name of a fragment point. The name used here must match one of the points in \$FRAGNAME. For the internally stored H2OEF2 and H2ODFT potential, the atom names are O1, H2, and H3.

X, Y, Z = Cartesian coordinates defining the position of this fragment point RELATIVE TO THE COORDINATE ORIGIN used in \$DATA. The choice of units is controlled by UNITS in \$CONTRL.

I, DISTANCE, J, BEND, K, TORSION = the usual Z-matrix connectivity internal coordinate definition. The atoms I, J, K must be atoms in the ab initio system from in \$DATA, or fragment points already defined in the current fragment or previously defined fragments.

Line -3- must be given a total of three times to define this fragment's position.

Repeat lines -2- and -3- to enter as many fragments as you desire, and then end the group with a \$END line.

Note that it is quite typical to repeat the same fragment name at line -2-, to use the same fragment system at many different positions.

* * * * *

For tips on effective fragment potentials
 see the 'further information' section

* * * * *

\$FRAGNAME group (required for each FRAGNAME given in \$EFRAG)

This group gives all pertinent information for a given effective fragment potential (EFP). This information falls into three categories:

electrostatic (distributed multipoles, screening)
distributed polarizabilities
exchange repulsion

It is input using several different subgroups, which should be given in the order shown below. Each subgroup is specified by a particular name, and is terminated by the word STOP. You may omit any of the subgroups to omit that term from the EFP. All values are given in atomic units.

To input monopoles,	follow input sequence -EM-
To input dipoles,	follow input sequence -ED-
To input quadrupoles,	follow input sequence -EQ-
To input octopoles,	follow input sequence -EO-
To input screening parameters,	follow input sequence -ES-
To input polarizable points,	follow input sequence -P-
To input repulsive points,	follow input sequence -R-

-1- a single descriptive title card

-2- COORDINATES

COORDINATES signals the start of the subgroup containing the multipolar expansion terms (charges, dipoles, ...). Optionally, one can also give the coordinates of the polarizable points, or centers of exchange repulsion.

-3- NAME, X, Y, Z, WEIGHT, ZNUC

NAME is a unique string identifying the point. X, Y, Z are the Cartesian coordinates of the point. WEIGHT and ZNUC are the atomic mass and nuclear charge, and are given only for the points which are nuclei.

Typically the true nuclei will appear twice, once for defining the positive nuclear charge and its screening, and a second time for defining the electronic distributed multipoles.

Repeat line -3- for each expansion point, and terminate the list with a "STOP".

-EM1- MONOPOLES

MONOPOLES signals the start of the subgroup containing the electronic and nuclear monopoles.

-EM2- NAME, CHARGE1, CHARGE2

NAME must match one given in the COORDINATES subgroup.

CHARGE1 = electronic monopole at this point.

CHARGE2 = nuclear monopole at this point. Omit or enter zero if this is a bond midpoint or some other expansion point that is not a nucleus.

\$FRAGNAME

Repeat -EM2- to define all desired charges. Terminate this subgroup with a "STOP".

-ED1- DIPOLES

DIPOLES signals the start of the subgroup containing the dipolar part of the multipolar expansion.

-ED2- NAME, MUX, MUY, MUZ

NAME must match one given in the COORDINATES subgroup. MUX, MUY, MUZ are the components of the electronic dipole.

Repeat -ED2- to define all desired dipoles.
Terminate this subgroup with a "STOP".

-EQ1- QUADRUPOLES

QUADRUPOLES signals the start of the subgroup containing the quadrupolar part of the multipolar expansion.

-EQ2- NAME, XX, YY, ZZ, XY, XZ, YZ

NAME must match one given in the COORDINATES subgroup. XX, YY, ZZ, XY, XZ, and YZ are the components of the electronic quadrupole moment.

Repeat -EQ2- to define all desired quadrupoles.
Terminate this subgroup with a "STOP".

-EO1- OCTUPOLES (note: OCTOPOLES is misspelled)

OCTUPOLES signals the start of the subgroup containing the octupolar part of the multipolar expansion.

-EO2- NAME, XXX, YYY, ZZZ, XXY, XXZ, XYY, YYZ, XZZ, YZZ, XYZ

NAME must match one given in the COORDINATES subgroup. XXX, ... are the components of the electronic octopole.

Repeat -EO2- to define all desired octopoles.
Terminate this subgroup with a "STOP".

-ES1- SCREEN

SCREEN signals the start of the subgroup containing the screening terms ($A \cdot \exp[-B \cdot r^2]$) for the distributed multipoles, which account for charge penetration effects.

-ES2- NAME, A, B

NAME must match one given in the COORDINATES subgroup. A, B are the parameters of the Gaussian screening term.

Repeat -ES2- to define all desired screening points.
 Terminate this subgroup with a "STOP".

-P1- POLARIZABLE POINTS

POLARIZABLE POINTS signals the start of the subgroup containing the distributed polarizability tensors, and their coordinates.

-P2- NAME, X, Y, Z

NAME gives a unique identifier to the location of this polarizability tensor. It might match one of the points already defined in the COORDINATES subgroup, but often does not. Typically the distributed polarizability tensors are located at the centroids of localized MOs.

X, Y, Z are the coordinates of the polarizability point. They should be omitted if NAME did appear in COORDINATES. The units are controlled by UNITS= in \$CONTRL.

-P3- XX, YY, ZZ, XY, XZ, YZ, YX, ZX, ZY

XX, ... are components of the distributed polarizability, which is not a symmetric tensor. XY means dM_{ux}/dF_y , where M_{ux} is a dipole component, and F_y is a component of an applied field.

Repeat -P2- and -P3- to define all desired polarizability tensors, and terminate this subgroup with a "STOP".

-R1- REPULSIVE POTENTIAL

See also the \$FRGRPL input group.

REPULSIVE POTENTIAL signals the start of the subgroup containing the fitted exchange repulsion potential, for the interaction between the fragment and the ab initio part of the system. This term also accounts for charge transfer effects. The term has the form

$$\sum_{i=1}^N C_i \exp[-D_i r_i^2]$$

-R2- NAME, X, Y, Z, N

NAME may match one given in the COORDINATES subgroup, but need not. If NAME does not match one of the known points, you must give its coordinates X, Y, and Z, otherwise omit these three values. N is the total number of terms in the fitted repulsive potential.

-R3- C, D

These two values define the i-th term in the repulsive potential. Repeat line -R3- for all N terms.

\$FRAGNAME

Repeat -R2- and -R3- to define all desired repulsive potentials, and terminate this subgroup with a "STOP".

The entire \$FRAGNAME group is terminated by a " \$END".

\$FRGRPL group

This group defines the inter-fragment repulsive potential, which consists primarily of exchange repulsions but also includes charge transfer. Note that the functional form used for the fragment-fragment repulsion differs from that used for the ab initio-fragment repulsion, which is defined in the \$FRAGNAME group. The form of the potential is

$$\sum_i^N A_i \exp[-B_i r]$$

-1- PAIR=FRAG1 FRAG2

specifies which two fragment repulsions are being defined. \$FRAGNAME input for the two names FRAG1 and FRAG2 must have been given.

-2- NAME1 NAME2 A B

or

NAME1 NAME2 'EQ' NAME3 NAME4

NAME1 must be one of the "NAME" points defined in the \$FRAG1 group's REPULSION POTENTIAL section. Similarly NAME2 must be a point from the \$FRAG2 group. In addition, NAME1 or NAME2 could be the keyword CENTER, indicating the center of mass of the fragment.

A and B are the parameters of the fitted repulsive potential.

The second form of the input allows equal potential fits to be used. The syntax implies that the potential between the points NAME1 and NAME2 should be taken the same as the potential previously given in this group for the pair of points NAME3 and NAME4.

If there are NPT1 points in FRAG1, and NPT2 points in FRAG2, input line -2- should be repeated NPT1*NPT2 times. Terminate the pairs of potentials with a "STOP" card. Any pairs which you omit will be set to zero interaction.

Typically the number of points on which fitted potentials might be taken to be all the nuclei in a fragment, plus the center of mass.

Repeat lines -1- and -2- for all pairs of fragments, then terminate the group with a \$END line.

\$PRTEFP group

(optional)

This group provides control for generating integer charge EFP fragments for constructing large EFPs. See

P.A.Molina, H.Li, J.H.Jensen J.Phys.Chem.B (2002) mss in preparation.

This group is mainly used in RUNTYP=MAKEFP runs. However, in MOPAC RUNTYP=ENERGY runs, the presence of a \$PRTEFP group causes AM1 or PM3 charges to be printed and punched out in a suitable format for EFP calculations.

NOPRT = an array specifying the atoms for which EFP multipole and polarizability points will not be printed/punched out.
Example: For a molecule with the connectivity A1-A2-A3-A4-A5, NOPRT(1)=4,5 means that multipoles centered on atoms 4 and 5, and bond midpoints BO34 and BO45 are not part of the EFP.

MIDPRT = an array specifying atoms whose bond midpoints neglected by using NOPRT should be printed out.
Example: MIDPRT(1)=3 forces the printout of bond midpoint BO34.

The neglect of monopoles leads to EFPs with overall non-integer charge. The next keyword defines "collection points" to which the removed monopoles are added. Thus, the net charge of the EFP=ICHARG. The presence of this "fictitious" charge is compensated for by adding an opposing dipole to the collection point.

NUMFFD = an array that defines (1) a collection point, (2) the number of atoms contributing to monopoles to this point, and (3) the numbers of the atoms. More than one collection point can be defined. An opposing dipole is calculated as $-0.5Q \cdot r$ (Q = sum of neglected monopoles, r = distance between collection point and nearest neglected monopole) and placed at the collection point.

Example: NUMFFD(1)=3,2,4,5. The sum of monopoles at A4, A5, BO34 and BO45 (Q) is added to the A3 monopole. A dipole, $-0.5Q \cdot r$, is placed on A3, where r is the distance between A3 and BO34. If MIDPRT(1)=3, Q does not include the BO34 monopole, r is the distance between BO34 and A4, and the resulting dipole is centered on BO34.

\$DAMP group (optional, relevant if RUNTYP=MAKEFP)

This group provides control over the screening of the distributed multipole expansion used by the EFP model for the electrostatic interaction, to account for charge penetration. See M.A.Freitag, M.S.Gordon, J.H.Jensen, W.A.Stevens, J.Chem.Phys. 112, 7300-7306(2000). The screening exponents are optimized by fitting a damped multipolar electrostatic potential to the actual quantum mechanical potential of the wavefunction. The fit is done on a Cartesian grid lying between inner and outer spheres on each atom. Two damping functions are generated. The first contains a single exponential form $(1 - \exp(a*r))$ where a varies, and initial guess values for a are given in \$DAMPGS. The second function is a single Gaussian form, $(1 - b*\exp(-a*r**2))$ where the initial values for a are taken from a STO-1G fit to the final values of the exponential fit. The exponential fit is used for fragment- fragment charge penetration screening, while the Gaussian fit is used in ab initio-fragment screening. See equations 28 and 4 in the reference. If \$DAMP is not given, the screening fit is skipped, an empty \$DAMP is sufficient to trigger a fit.

- VDWRAD = an array of van der Waals radii for each atom in the molecule. Defaults are taken from Emsley's yellow book, "The Elements" so are not built in for exotic elements like transition metals.

- RMIN1 = the minimum radius scale factor for each atom, for the Gaussian fitting steps. (default=0.67)

- RMAX1 = the maximum radius scale factor for each atom, for the Gaussian fitting steps. (default=3.00)

- RMIN2 = the minimum radius scale factor for each atom, for the exponential fittings. The reference paper suggests use of 67% of the van der Waals radius. (default=0.67)

- RMAX2 = the maximum radius scale factor for each atom, for the exponential fittings. The reference paper suggests use of 300% of the van der Waals radius. (default=3.00)

- XGRID = spacing between grid points (default = 0.5 a.u.)

- MAXIT = maximum number of iterations in the fitting step. The default is 10000.

- THRSH = printing threshold for large deviations. The default is 4.0 kcal/mol.

\$DAMPGS

(relevant if \$DAMP was given)

This is a free-format, line by line input group that sets the initial values (guess) for the exponential damping function used to screen the multipole expansion. The initial guess for the Gaussian fit is taken from the final values of the exponential fit, once that is done.

Each multipole expansion point (typically all atoms followed by all bond midpoints) should receive a value. A check run may be helpful in listing the names of the expansion points that are chosen by MAKEFP jobs.

```
-1-    <exp.pt.> <nterms>
      <exp.pt.> 'EQ' <prev.exp.pt.>
```

This line gives the name of the expansion point, and how many terms are in the damping function. You must enter 1 for the number of terms. The second form of this line lets you equate the current point to some previous point's values in \$DAMPGS, skipping line -2-.

```
-2-  <coef> <exponent> <ifreeze>
```

The linear coefficient and exponent of this term in the damping function. Repeat input for -2- <nterms> times. You must enter the coefficient as 1.0 at the present. If the integer <ifreeze> is omitted or given as 0, the exponents are optimized, but entering 1 freezes these.

Repeat -1- and -2- until all multipole centers receive their initial guess parameters.

\$PCM group (optional)

This group controls solvent effect computations using the Polarizable Continuum Model. If this group is found in the input file, a PCM computation is performed. The default calculation, chosen by selecting only the SOLVNT keyword, is to compute the electrostatic free energy. Appropriate numerical constants are provided for a wide range of solvents. Additional keywords allow for more sophisticated computations, namely cavitation, repulsion, and dispersion free energies. The methodology for these is general, but only numerical constants for water are provided. There is additional information on PCM in the References chapter of this manual.

PCM is programmed only for RHF and MCSCF wavefunctions.

Tight geometry optimization with PCM might not be able to converge to the OPTTOL values below the default \$STATPT. Use of GEPOL-RT tessellation may result in crisper geometry convergence at some cost in machine time, see \$TESCAV.

--- the first set of parameters controls the computation:

IEF, ICOMP, ICAV, IDISP, IREP, IDP, and IFIELD.

- IEF switch to choose the type of PCM model used.
- = 0 isotropic dielectrics using D-PCM
 - = 1 anisotropic dielectrics using IEF PCM, see \$IEFPCM
 - = 2 ionic solutions using IEF PCM, see \$IEFPCM
 - = 3 isotropic dielectrics using IEF PCM with matrix inversion solver, see IEFPCM
 - = -3 isotropic dielectric IEF PCM with iterative solver, see \$PCMITR. Note that IEF=-3 usually reproduces the energy of IEF=3 to within 1.0d-5 Hartrees, but is much faster for large molecules.
 - = 10 conductor-like PCM (C-PCM) with matrix inversion. charge scaling factor=(Eps-1.0)/Eps
 - = -10 C-PCM, with iterative solver. See \$PCMITR.

The default is 3 for energy calculations, but -3 for gradients.

The value of IPCDER in \$PCMGRD controlling the gradient computational method is related to IEF, according to

IEF= 3 may choose only IPCDER=0,1

IEF=-3 may choose from IPCDER=0,1,2

The behaviour of PCM prior to Oct. 2000 can be recovered by selecting IEF=0 and ICOMP=2. Options IEF=1 or 2 are incompatible with gradients and also must choose ICOMP=0. IEF=3 may not choose ICOMP=3, but if diffuse functions are in use, this IEF choice may benefit from ICOMP=2. The D-PCM method (IEF=0) should normally choose ICOMP=2.

*** at the present time, there is a bug with IEF=1 or 2.

- ICOMP = Compensation procedure for induced charges.
 Gradient runs require ICOMP be 0 or 2 only.
- = 0 No. (default)
 - = 1 Yes, each charge is corrected in proportion to the area of the tessera to which it belongs.

- = 2 Yes, using the same factor for all tesserae.
- = 3 Yes, with explicit consideration of the portion of solute electronic charge outside the cavity, by the method of Mennucci and Tomasi. See the \$NEWCAV group.

- ICAV
- = At the end of the run, calculate the cavitation energy, by the method of Pierotti and Claverie:
 - = 0 skip the computation (default)
 - = 1 perform the computation.

If ICAV=1, the following parameter is relevant:

- TABS = the absolute temperature, in units K. (default=298.0)

There are two procedures for the calculation of the repulsion and dispersion free energy. IDISP is incompatible with IREP and IDP.

- IDISP
- = Calculation of both dispersion and repulsion free energy through the empirical method of Floris and Tomasi.
 - = 0 skip the computation (default)
 - = 1 perform the computation. See \$DISREP group.

The next two options add repulsive and dispersive terms to the solute hamiltonian, in an ab initio manner, by the method of Amovilli and Mennucci.

- IREP
- = Calculation of repulsion free energy
 - = 0 skip the computation (default)
 - = 1 perform the computation. See \$NEWCAV group.

- IDP
- = Calculation of dispersion free energy
 - = 0 skip the computation (default)
 - = 1 perform the computation. See \$DISBS group.

If IDP=1, then three additional parameters must be defined. The two solvent values correspond to water, and therefore these must be input for other solvents.

- WA = solute average transition energy. This is computed from the orbital energies for RHF, but must be input for MCSCF runs. (default=1.10)
- WB = ionization potential of solvent, in Hartrees. (default=0.451)
- ETA2 = square of the zero frequency refractive index of the solvent. (default=1.75)
- IFIELD
- = At the end of a run, calculate the electric potential and electric field generated by the apparent surface charges.
 - = 0 skip the computation (default)
 - = 1 on nuclei
 - = 2 on a planar grid

If IFIELD=2, the following data must be input:

- AXYZ,BXYZ,CXYZ = each defines three components of the vertices of the plane where the reaction field is to be computed (in Angstroms)

A ==> higher left corner of the grid
B ==> lower left corner of the grid
C ==> higher right corner of the grid
NAB = vertical subdivision (A--B edge) of the grid
NAC = horizontal subdivision (A--C edge) of the grid.

--- the next group of keywords defines the solvent

SOLVNT = keyword naming the solvent of choice. The eight numerical constants defining the solvent are internally stored for the following:

WATER (or H2O)	
CH3OH	C2H5OH
CLFORM (or CHCl3)	CTCL (or CCl4)
METHYCL (or CH2Cl2)	12DCLET (or C2H4Cl2)
BENZENE (or C6H6)	TOLUENE (or C6H5CH3)
CLBENZ (or C6H5Cl)	NITMET (or CH3NO2)
NEPTANE (or C7H16)	CYCHEX (or C6H12)
ANILINE (or C6H5NH2)	ACETONE (or CH3COCH3)
THF	DMSO (or DMETSOX)

The default solvent name is "INPUT" which indicates you are giving the following 8 numerical values:

RSOLV = the solvent radius, in units Angstrom
EPS = the dielectric constant
EPSINF = the dielectric constant at infinite frequency.
This value must be given only for RUNTYP=TDHF, if the external field frequency is in the optical range and the solvent is polar; in this case the solvent response is described by the electronic part of its polarization. Hence the value of the dielectric constant to be used is that evaluated at infinite frequency, not the static one (EPS). For nonpolar solvents, the difference between the two is almost negligible.
TCE = the thermal expansion coefficient, in units 1/K
VMOL = the molar volume, in units ml/mole
STEN = the surface tension, in units dyne/cm
DSTEN = the thermal coefficient of log(STEN)
CMF = the cavity microscopic coefficient

Values for TCE, VMOL, STEN, DSTEN, CMF need to be given only for the case ICAV=1. Input of any or all of these values will override the internally stored value.

--- the next set of keywords defines the molecular cavity

NESFP = the number of initial spheres. (default = number of atoms in solute molecule)
ICENT = option for definition of initial spheres.
= 0 centers spheres on each nucleus. (default)
= 1 sphere centers XE, YE, ZE and radii RIN will be specified explicitly in \$PCMCAY.

The cavity generation algorithm may use additional spheres to smooth out sharp grooves, etc. The following parameters control how many extra spheres are generated:

OMEGA and FRO = GEPOL parameters for the creation of the 'added spheres' defining the solvent accessible surface. When an excessive number of spheres is created, which may cause problems of convergence, the value of OMEGA and/or FRO must be increased. For example, OMEGA from 40 to 50 ... up to 90, FRO from 0.2 ... up to 0.7. (defaults are OMEGA=40.0, FRO=0.7)

RET = minimum radius (in Å) of the added spheres. Increasing RET decreases the number of added spheres. A value of 100.0 (default) inhibits the addition of any spheres, while 0.2 fills in many.

IPRINT = 0 normal printing (default)
= 1 turns on debugging printout

\$PCMGRD group (optional)

This group controls the PCM gradient computations.

- IPCDER = selects different methods for PCM gradients
- = 0 fixed-cavity approximation Implemented only for C-PCM and IEF-PCM
 - 1 use $U_x(q)$ approximation (C-PCM and IEF-PCM) or use charge-derivative method (D-PCM). This is the default for D-PCM
 - 2 Variable-Tessera-Number Approximation Implemented only for C-PCM and IEF-PCM, and the default for both of these.

note: If ICAV = 1 or IDISP = 1 in \$PCM, the derivatives of the cavitation energy or dispersion-repulsion, respectively, will automatically be calculated. These particular steps are evaluated numerically.

- IFAST = Controls the PCM calculations for RUNTYP=OPTIMIZE.
- 0 update PCM charges at each SCF cycle at every geometry (default)
 - 1 update PCM charges at each SCF cycle for the initial geometry. For the subsequent geometries, calculate PCM charges at the first SCF cycle and use the PCM charges for the following SCF cycles; after the density change falls below DENTOL, update the PCM charges one time (to save CPU time).

\$PCMCAV group (optional)

This group controls generation of the cavity holding the solute during Polarizable Continuum Model runs. The cavity is a union of spheres, according to ICENT and associated input values given in \$PCM. The data given here must be given in Angstrom units.

XE,YE,ZE = arrays giving the coordinates of the spheres.
 if ICENT=0, the atomic positions will be used.
 if ICENT=1, you must supply NESFP values here.

- RADII = VANDW selects van der Waals radii (Angstrom), which is the default.
 VDW radii for atoms
 H,He, B,C,N,O,F,Ne, Na,Al,Si,P,S,Cl,Ar,
 K,As,Se,Br,Kr, Rb,Sb,Te,I, Cs,Bi
 are internally tabulated, for others give RIN.
- = VDWEFP, similar to VANDW, except that radii not tabulated by VANDW are assigned as 1.60A. This option is most useful for protein-EFP calculations.
- = SUAEPF, the simplified united atomic radii will be used for the array RIN, namely
 H:0.01 C:1.77 N:1.68 O:1.59 P:2.10 S:2.10
 For the other elements with $Z < 16$, 1.50 will be used.
 For the elements with $Z > 16$, 2.30 will be applied.
 This is for the purpose of protein EFP calculations

note: Radii explicitly defined with RIN will overwrite the defaults selected by VANDW, VDWEFP, or SUAEPF.

RIN = an array giving the sphere radii.

if ICENT=0, the program will look up the internally stored data according to the RADII keyword.

if ICENT=1, give NESFP values.

ALPHA = an array of scaling factors, for the definition of the solvent accessible surface. If only the first value is given, all radii are scaled by the same factor. (default is ALPHA(1)=1.2)

Example: Suppose the 4th atom in your molecule is Fe, but all other atoms have van der Waals radii. You decide a good guess for Fe is twice the covalent radius:

\$PCMCAV RIN(4)=2.33 \$END

The source for the van der Waals radii is "The Elements", 2nd Ed., John Emsley, Clarendon Press, Oxford, 1991 , except that for C,N,O, the U.Pisa's experience with the best radii for PCM treatment of singly bonded C,N,O atoms is used instead. The radii for a few transition metals are given by A.Bondi, J.Phys.Chem. 68, 441-451(1964).

\$TESTCAV group (optional)

This group controls the tessellation procedure for the molecular surface in the PCM computations. The default values for this group will normally be satisfactory. To converge to smaller OPTTOL values may take a high density of tessera on the cavity surface:

MTHALL=3 NTSALL=960 AREATL=0.0010 BONDRY=1000.0

This set of options may require raising the maximum number of tessera, MXTS in the source code (see PROG.DOC). It is reasonable to try just MTHALL=3 first, as this may be sufficient w/o increasing the tessera density. See also IFAST=1 in \$PCMGRD.

--- The first two arrays control the density of tesserae and the method to generate the tesserae.

- INITS = array defines the initial number of tesserae for each sphere. Only 60, 240 and 960 are allowed, but the value can be different for each sphere. (Default=60 for all spheres)
- METHOD = array defining the tessellation method for each sphere. Only 1 and 3 are allowed, but the value can be different for each sphere. The default is 1 for all spheres.
- = 1 GEPOL-GB, "Gauss-Bonet" tessellation
 - = 3 GEPOL-RT, "regular tessellation".

--- The next three parameters are presets for filling the arrays INITs and METHOD

- NTSALL = 60, 240 or 960 (default = 60) All values in the array INITs are set to NTSALL
- MTHALL = 1 or 3 (default = 1)
All values in the array METHOD are set to MTHALL
- MTHAUT = 0 or 1 (default = 0)
If RUNTYP=OPTIMIZE and frozen atoms are defined by IFCART,
MTHAUT=1 will select METHOD=1 for frozen atoms. See also AUTFRE and NTSFRZ

note: Explicitly defining INITs and METHOD from the input deck will overrule the presets from NTSALL, MTHALL and/or MTHAUT.

--- The following two parameters control GEPOL-RT

- AREATL = The area criterion (A^2) for GEPOL-RT. Tesserae with areas $< AREATL$ at the boundary of intersecting spheres will be neglected. Default=0.010 A^2 . Smaller AREATL cause larger number of tesserae. $AREATL < 0.00010$ is not recommended
- BONDRY = Controls (by scaling) the distance within which tesserae are considered "close" to the boundary. Such tesserae will be recursively divided into smaller ones until their areas are $< AREATL$. The default (= 1.0) means the distance is the square root of the tessera area. A large BONDRY value like 1000.0 will lead to fine tessellation for the entire surface with all tessera areas $< AREATL$.

\$TESTCAV, \$NEWCAV, \$IEFPCM

--- The next two parameters are only relevant if MTHAUT=1

AUTFRE = Distance (A) for frozen atoms to be treated as moving atoms when MTHAUT=1. Default=2.0 A.

NTSFRZ = 60, 240 OR 960, initial tessera number for frozen atoms. Default=60

\$NEWCAV group (optional)

This group controls generation of the "escaped charge" cavity, used when ICOMP=3 or IREP=1 in \$PCM. This cavity is used only to calculate the fraction of the solute electronic charge escapes from the original cavity.

IPTYPE = choice for tessalation of the cavity's spheres.
 = 1 uses a tetrahedron
 = 2 uses a pentakis dodecahedron (default)

ITSNUM = m, the number of tessera to use on each sphere.
 if IPTYPE=1, input $m=30*(n^2)$, with $n=1,2,3$ or 4
 if IPTYPE=2, input $m=60*(n^2)$, with $n=1,2,3$ or 4
 (default is 60)

*** the next three parameters pertain to IREP=1 ***

RHOW = density, relative to liquid water (default = 1.0)

PM = molecular weight (default = 18.0)

NEVAL = number of valence electrons on solute (default=8)

The defaults for RHOW, PM, and NEVAL correspond to water, and therefore must be correctly input for other solvents.

\$IEFPCM group (optional)

This group defines data for the integral equation formalism version of PCM solvation. It includes special options for ionic or anisotropic solutions.

The next two sets are relevant only for anisotropic solvents, namely IEF=1:

EPS1, EPS2, EPS3 =
 diagonal values of the dielectric permittivity tensor with respect to the laboratory frame.
 The default is EP1, 2, 90S in \$PCM

EUPHI, EUTHE, EUPSI =
 Eulerian angles which give the rotation of the solvent orientation with respect to the lab frame. The term lab frame means \$DATA orientation. The default for each is zero degrees.

The next two are relevant to ionic solvents, namely IEF=2:

EPSI = the ionic solutions's dielectric, the default is EPS from \$PCM.

DISM = the ionic strength, in Molar units (mol/dm^3)
The default is 0.0

\$PCMITR group (optional, for IEF=-3 in \$PCM)

This group provides control over the iterative isotropic IEF-PCM calculation. See
 C.S.Pomelli, J.Tomasi, V.Barone Theoret.Chem.Acc. 105, 446-451(2001)
 H.Li, C.S.Pomelli, J.H.Jensen Theoret.Chem.Acc. 109, 71-84(2003)

MXDIIS = Maximum size of the DIIS linear equations, the value impacts the amount of memory used by PCM.
 Memory=2*MXDIIS*NTS, where NTS is the number of tesserae.
 MXDIIS=0 means no DIIS, instead the point Jacobi iterative method will be used. (Default=50)

MXITR1 = Maximum number of iters in phase 1. (Default=50)

MXITR2 = Maximum number of iters in phase 2. (Default=50)

note: if MXDIIS is larger than both MXITR1 and MXITR2 MXDIIS will be reset to be the larger of these two.

THRES = Convergence threshold for the PCM Apparent Surface Charges (ASC).
 (Default=1.0D-08)

THRSLS = Loose threshold used in the early SCF cycles when the density change is above DENSLS. If THRSLS < THRESH, this option is turned off. Default is 5.0D-04.

DENSLS = If the density change is above DENSLS the loose threshold THRSLS applies.
 (Default = 0.01 au)

IDIRCT = 1, Directly compute the electronic potential at each tessera and the ASC potential at the electronic coordinates, with no disk storage. (Default)
 0, Compute and save above data to hard disk.

Keywords for region wise multipole expansion of ASCs in approximating interaction among tesserae:

(C.S.Pomelli, J.Tomasi THEOCHEM 537, 97-105(2001))

IMUL = Region wise multipole expansion order in the approximate interaction among tesserae.
 = 0, Neglected (Only for test purposes)
 = 1, Monopole
 = 2, Monopole+Dipole
 = 3, Monopole+Dipole+Quadrupole (Default)

RCUT1 = Cutoff radius (Angstrom) for mid-range interactions among tesserae.
 Default=15.0 A If RCUT1 is larger than your molecule, the option is effectively turned off.

RCUT2 = Cutoff radius (Angstrom) for long range interactions among tesserae.

Default=30.0 A

The remaining keywords apply only to PCM calculations with a QM/EFP solute (see Li et al.)

Keywords for region wise multipole expansion of ASCs in approximating interaction between ASCs and QM region:

IMGASC = 1, Use region wise multipole expansion of ASCs to compute the ASC potential at QM region.
0, no use of the multipole expansion method. (default)

RASC = Cutoff radius (Angstrom) for used of the IMGASC multipole expansion (Default=20.0 A)

Keywords for multipole expansion of the QM region in approximating the QM region potential:

IMGABI = 0, multipole expansion of the QM region is turned off (default).
1, turn multipole expansion of the QM region on.

RABI = Cutoff radius (Angstrom) for used of the IMGABI multipole expansion (Default=4.0 A)

Keywords for the coupling of PCM and EFP polarizability tensors:

IEFPOL = 1, PCM ASCs induce EFP dipoles.(default)
0, PCM ASCs do not induce EFP dipoles.

REFPOL = When IEFPOL=1, if the distance (Angstrom) between a polarizability point and a tessera is less than REFPOL, they are considered too close and the field from the tessera will not induce dipole for the polarizability point. Default=0.0 A means always induce the dipole.

\$DISBS group

(optional)

This group defines auxiliary basis functions used to evaluate the dispersion free energy by the method of Amovilli and Mennucci. These functions are used only for the dispersion calculation, and thus have nothing to do with the normal basis given in \$BASIS or \$DATA. If the input group is omitted, only the normal basis is used for the IDP=1 dispersion energy.

NADD = the number of added shells

XYZE = an array giving the x,y,z coordinates (in bohr) of the center, and exponent of the added shell, for each of the NADD shells.

NKTYPE = an array giving the angular momenta of the shells

An example placing 2s,2p,2d,1f on one particular atom,

```
$DISBS  NADD=7  NKTYP(1)= 0 0 1 1 2 2 3
      XYZE(1)=2. 9281086    0. 0    .0001726    0. 2
              2. 9281086    0. 0    .0001726    0. 05
              2. 9281086    0. 0    .0001726    0. 2
              2. 9281086    0. 0    .0001726    0. 05
              2. 9281086    0. 0    .0001726    0. 75
              2. 9281086    0. 0    .0001726    0. 2
              2. 9281086    0. 0    .0001726    0. 2  $END
```

\$DISREP group (optional)

This group controls evaluation of the dispersion and repulsion energies by the empirical method of Floris and Tomasi. The group must be given with IDISP=1 in \$PCM. The two options are controlled by ICLAV and ILJ, only one of which should be selected.

- ICLAV = selects Claverie's disp-rep formalism.
 = 0 skip computation.
 = 1 Compute the solute-solvent disp-rep interaction as a sum over atom-atom interactions through a Buckingham-type formula (R^{-6} for dispersion, \exp for repulsion). (Default) Ref: Pertsin-Kitaigorodsky "The atom-atom potential method", page 146.
- ILJ = selects a Lennard-Jones formalism.
 = 0 skip computation. (default)
 = 1 solute atom's-solvent molecule interaction is modeled by Lennard-Jones type potentials, R^{-6} for dispersion, R^{-12} for repulsion).

---- the following data must given for ICLAV=1:

- RHO = solvent numeral density
 N = number of atom types in the solvent molecule
 NT = an array of the number of atoms of each type in a solvent molecule
 RDIFF = distances between the first atoms of each type and the cavity
 DKT = array of parameters of the dis-rep potential for the solvent
 RWT = array of atomic radii for the solvent

The defaults are chosen for water,

RHO=3.348D-02
 N=2
 NT(1)=2,1
 RDIFF(1)=1.20,1.50
 DKT(1)=1.0,1.36
 RWT(1)=1.2,1.5

- DKA = array of parameters of the dis-rep potential for the solute. Defaults are provided for some common elements:
 H: 1.00 Be: 1.00 B: 1.00 C: 1.00
 N: 1.10 O: 1.36 P: 2.10 S: 1.40
- RWA = array of atomic radii for the solute to compute dis-rep. Defaults are provided for some common elements:
 H: 1.20 Be: 1.72 B: 1.72 C: 1.72
 N: 1.60 O: 1.50 P: 1.85 S: 1.80

Other elements have DKA and RWA values of 0.0 and must be given in the input deck, or the DIS-REP energy will be 0. For EFP/PCM calculations, only QM atoms need DKA and RWA values to calculate the DIS-REP energy.

---- the following data must given for ILJ=1:

- RHO = solvent numeral density

EPSI = an array of energy constants referred to each atom of the solute molecule.
SIGMA = an array of typical distances, relative to each solute atom

\$COSGMS group (optional)

The presence of this group in the input turns on the use of the conductor-like screening model with molecular shaped cavity for RHF and closed shell MP2. For RHF, the energy and gradient can be computed, while MP2 is limited to the energy only.

- EPSI = the dielectric constant, 80 is often used for H₂O This parameter must be given.
- RSOLV = the multiplicative factor for the van der Waals radius used for cavity construction. (default=1.2)
- NSPA = the number of surface points on each atomic sphere that form the cavity. (default=92)

Additional information on the COSMO model can be found in the References chapter of this manual.

\$SCRF group (optional)

The presence of this group in the input turns on the use of the Kirkwood-Onsager spherical cavity model for the study of solvent effects. The method is implemented for RHF, UHF, ROHF, GVB and MCSCF wavefunctions and gradients, and so can be used with any RUNTYP involving the gradient. The method is not implemented for MP2, CI, any of the semiempirical models, or for analytic Hessians.

- DIELEC = the dielectric constant, 80 is often used for H₂O
- RADIUS = the spherical cavity radius, in Angstroms
- G = the proportionality constant relating the solute molecule's dipole to the strength of the reaction field. Since G can be calculated from DIELEC and RADIUS, do not give G if they were given.

Additional information on the SCRF model can be found in the References chapter of this manual.

\$ECP group (required if ECP=READ in \$CONTRL)

This group lets you read in effective core potentials, for some or all of the atoms in the molecule. You can use built in potentials for some of the atoms if you like. This is a free format (positional) input group.

*** Give a card set -1-, -2-, and -3- for each atom ***

-card 1- PNAME, PTYPE, IZCORE, LMAX+1

PNAME is a 8 character descriptive tag for this potential. If it is repeated for a subsequent atom, no other information need be given on this card, and cards -2- and -3- may also be skipped. The information will be copied from the first atom by this PNAME. Do not use the option to repeat the previously read ECP for an atom with PTYPE=NONE, instead type "NONE" over and over again.

PTYPE = GEN a general potential should be read.
 = SBKJC look up the Stevens/Basch/Krauss/Jasien/ Cundari potential for this type of atom.
 = HW look up the Hay/Wadt built in potential for this type of atom.
 = NONE treat all electrons on this atom.

IZCORE is the number of core electrons to be removed. Obviously IZCORE must be an even number, or in other words, all core orbitals being removed must be completely occupied.

LMAX is the maximum angular momentum occupied in the core orbitals being removed (usually). Give IZCORE and LMAX only if PTYPE is GEN.

*** For the first occurrence of PNAME, if PTYPE is GEN, ***
 *** then give cards -2- and -3-. Otherwise go to -1-. ***

*** Card sets -2- and -3- are repeated LMAX+1 times ***

The potential $U(LMAX+1)$ is given first, followed by $U(L)-U(LMAX+1)$, for $L=1,LMAX$.

-card 2- NGPOT

NGPOT is the number of Gaussians in this part of the local effective potential.

-card 3- CLP,NLP,ZLP (repeat this card NGPOT times)

CLP is the coefficient of this Gaussian in the potential.
 NLP is the power of r for this Gaussian.
 ZLP is the exponent of this Gaussian.

Note that PTYPE lets you to type in one or more atoms explicitly, while using built in data for other atoms.

By far the easiest way to use the SBKJC potential for all atoms in the formic acid molecule is to request ECP=SBKJC in \$CONTRL. But here we show two alternatives.

The first way is to look up the program's internally stored SBKJC potentials one atom at a time:

```
$ECP
C- ECP SBKJC
H- ECP NONE
O- ECP SBKJC
O- ECP
H- ECP NONE
$END
```

The second oxygen duplicates the first, no core electrons are removed on hydrogen. The order of the atoms must follow that generated by \$DATA. All atoms must be given here in \$ECP, not just the symmetry unique atoms.

The second example reads all SBKJC potentials explicitly:

```
$ECP
C- ECP GEN 2 1
1      ----- CARBON U(P) -----
-0. 89371  1  8. 56468
2      ----- CARBON U(S) - U(P) -----
1. 92926  0  2. 81497
14. 88199  2  8. 11296
H- ECP NONE
O- ECP GEN 2 1
1      ----- OXYGEN U(P) -----
-0. 92550  1 16. 11718
2      ----- OXYGEN U(S) - U(P) -----
1. 96069  0  5. 05348
29. 13442  2 15. 95333
O- ECP
H- ECP NONE
$END
```

Again, the 2nd oxygen copies from the first. It is handy to use the rest of card - 2- as a descriptive comment.

As a final example, for antimony we have LMAX+1=3 (there are core d's). One must first enter U(f), followed by U(s)-U(f), U(p)-U(f), U(d)-U(f).

\$MCP group (required if MCP READ was given on card -6U-)

This group lets you read in model core potentials, for some or all of the atoms in the molecule. This is a fixed format input group. For the review of the MCP method, see M.Klobukowski, Y.Sakai, and S.Huzinaga, pp. 49-74 in J. Leszczynski, "Computational Chemistry", vol. 3 (1999) .

*** Give input -1-, -2-, ..., -9- for each MCP atom ***

-card 1- ANAT

ANAT is a 8 character name for the MCP atom. It must match the name given for that atom in the \$DATA group.

-card 2- NOAN, (NO(IS),NG(IS), IS=1,4) FORMAT(9I3)
IS = 1, 2, 3, 4 for s, p, d, and f symmetry, resp.

NOAN is the number of terms in the MCP

NO(IS) is the number of core orbitals in symmetry IS

NG(IS) is the number of basis functions used to expand the core orbitals in symmetry IS

-card 3- ZEFF, MCPFMT FORMAT(F10.2, A8)

ZEFF is the number of valence electrons, e.g. 7.0 for Fluorine

MCPFMT is the format for reading floating-point numbers in the MCP data

-card 4- (ACOE(L), L=1,NOAN) FORMAT(MCPFMT)

ACOE(L) is the L-th coefficient in the expansion of the model core potential; more than one line may be provided

ACOE(L) is defined as A(l) in Eq. (38) of the MCP review paper.

-card 5- (AEXP(L), L=1,NOAN) FORMAT(MCPFMT)

AEXP(L) is the L-th exponent in the expansion of the model core potential; more than one line may be provided

AEXP(L) is defined as $\alpha(l)$ in Eq. (38) of the MCP review paper.

-card 6- (NINT(L), L=1,NOAN) FORMAT(10I3)

NINT(L) is the power of R in the expansion of the model core potential; NINT(L) is defined as n(l) in Eq. (38) of the MCP review paper.

*** For each symmetry IS present in the core orbitals ***

*** read the card set -7-, -8-, and -9- ***

-card 7- (BPAR(K), K=1,NO(IS)) FORMAT(MCPFMT)

BPAR(K) is the constant in the core projector operator, B(k) in Eq. (41) of the review.

-card 8- (EX(I), I=1,NG(IS)) FORMAT(MCPFMT)

EX(I) is the exponent of the I-th Gaussian function used to expand the core orbitals

*** Repeat -9- for each core orbital in symmetry IS ***

-card 9- (C(I), I=1,NG(IS)) FORMAT(MCPFMT)
C(I) expansion coefficients of the core orbital

The following example input file is for H2CO, and by the way, provides another example of COORD=HINT.

```

!
$CONTRL RUNTYP=ENERGY COORD=HINT ECP=MCP $END
$DATA
Formaldehyde H2CO
CNV 2

C 6.0 LC 0.00 0.0 0.0 - O K
MCP READ <<<< this is an MCP atom
L 3 <<<< (311/311/1) basis
1 18.517235 -0.16370140 0.22673090E-01
2 2.5787547 -0.26304451 0.19109693
3 0.58994362 0.58040872 0.50918856
L 1
1 0.17330638 1.0000000 1.0000000
L 1
1 0.60957120E-01 1.0000000 1.0000000
D 1; 1 0.600 1.0

O 8.0 LC 1.2031 0.0 0.0 - O K
MCP READ <<<< this is an MCP atom
L 3 <<<< (311/311/1) basis
1 44.242510 -0.13535836 0.17372951E-01
2 6.2272700 -0.30476423 0.16466813
3 1.4361751 0.43955753 0.46721611
L 1
1 0.40211473 1.0000000 1.0000000
L 1
1 0.12688798 1.0000000 1.0000000
D 1; 1 1.154 1.0

H 1.0 PCC 1.1012 121.875 0.0 + O K I
TZV <<<< not an MCP atom, TZV+pol basis
P 1; 1 1.100 1.0

$END

$MCP <<<< start of the MCP data
<<<< empty lines allowed
MCP for C NR (2S/2P) S(2)P(2) <<<< comment
<<<< empty lines allowed
C <<<< MCP for the atom C
2 1 14 <<<< NOAN, NO(1), NG(1)
4.00(4D15.8) <<<< ZEFF, MCPFMT

```

2-120

\$MCP

```
.41856306 .99599513E-01 <<<< ACOEF
16.910482 7.4125554 <<<< AEXPN
O O <<<< NINT
22.676882 <<<< B(1s)
26848.283 8199.1206 2798.3668 1048.2982
423.36984 181.26843 81.068295 37.403931
17.629539 8.4254263 4.0611964 1.9672294
.95541420 .46459041
.10743274D-03 .21285491D-03 .99343100D-03 .28327774D-02
.83154481D-02 .21694082D-01 .52916004D-01 .11618593D+00
.21812785D+00 .32180986D+00 .29375407D+00 .10974353D+00
.70844050D-02 .17825971D-02
```

MCP for O NR (2S/2P) S(2)P(4)

```
O <<<< MCP for the atom O
2 1 16
6.00(4D15.8)
.31002267 .27178756E-01
25.973731 13.843290
O O
41.361784
57480.749 17270.167 5766.9282 2107.0076
829.06758 346.04791 151.12147 68.233250
31.542773 14.815300 7.0298236 3.3561489
1.6077662 .77153240 .37052330 .17799002
.85822477D-04 .18173691D-03 .84803428D-03 .25439914D-02
.76877460D-02 .20823429D-01 .52424753D-01 .11864010D+00
.22782741D+00 .33492260D+00 .28833079D+00 .93046197D-01
.55937988D-02 .16121923D-02 .10915544D-04 .21431633D-03
```

\$END

\$RELWFN group

(optional)

This group is relevant if RELWFN in \$CONTRL chose the NESC or RESC option for elimination of small components from relativistic wavefunctions, to produce a corrected single component wavefunction. In case of RESC, only the one electron integral corrections are added, whereas for NESC, corrections to two electron integrals are accounted for by means of a relativistically averaged basis set.

Analytic gradients are programmed for both RESC and NESC computations. For NESC, the one electron part of the spin-orbit operator can be corrected, while for RESC, one can compute spin-orbit coupling with relativistic corrections to both one and two electron SOC integrals, unless internal uncontraction is requested. In this case only one electron SOC integrals are modified. It should be noted that internally uncontracted basis functions with very large exponents have large SOC integrals, thus the average asymmetry due to RESC appears to be larger (before contraction).

For NESC, you must provide three basis sets, for the large and small components and an averaged one, which are given in \$DATAL, \$DATAS, \$DATA, respectively. The only possible choice for these basis sets is due to Dyll, and these are available from:

<http://www.emsl.pnl.gov:2080/forms/basisform.html>

Their names are similar to cc-pVnZ(pt/sf/lc), pt=point or fi=finite nucleus, sf for spin-free and the final field is lc=large component (\$DATAL), sc=small component (\$DATAS), and wf is a typo for Foldy-Wouthuysen 2e- basis (\$DATA). In GAMESS you can only use point nucleus approximation. The need to input three basis sets means that you cannot use a \$BASIS group, and you must use COORD=UNIQUE style input in the various \$DATA's. The three \$DATA groups must contain identical information except for the primitive expansion coefficients, as the three basis sets must have the same exponents. In case the option to treat only some atoms relativistically is chosen, all non-relativistic atoms must have identical basis input in all three groups.

For RESC, ordinary basis sets are used. This however is a misleading statement, for while any basis set will run, accurate answers may be hard to obtain without the use of basis sets contracted using the RESC approximation. Experience is showing that large uncontracted basis sets using non-relativistic exponents are probably OK, but that standard contractions of these in NR calculations can lead to spurious results. Unfortunately, contractions using the RESC approximation are not yet available for ordinary use.

OPRESC gives additive (bitwise) options, which pertain to the RESC method:

- = 0 original RESC implementation, reproduces the results prior to June 2001. The accuracy of the RI may be inadequate. (default)
- = 1 to obtain more accurate integrals, use the Gaussian primitives rather than the contracted basis set to define the resolution of the identity (RI), used to simplify the integrals in order to evaluate them in closed form. This internally uncontracted basis set can be large, but produces considerably increased accuracy in the integrals (see also NRATOM/CHARGE).
- = 2 HONDO's implementation of the RI for RESC is mimicked, namely that for ISPHER=+1 the space used for the RI will not have spherical contaminants (similarly to MO space). No gradients for HONDO style are available.

- = 4 split L-shells into s and p when generating the internally uncontracted basis set. This is necessary if you are using s or p primitives with the same exponents declared as some L shell. In such a case, the L shell must be entered before the s or p. 4 requires 1.

These options are additive, for example OPRESC=5 is needed to select 1 as well as 4.

- NESOC = relativistic corrections to SOC integrals. Choose only if RELWFN=RESC or NESC, and if OPERAT=HSO1, HSO2P, or HSO2, for RUNTYP=TRANSITN
- = 0 no corrections
 - = 1 one-electron spin-orbit integrals (NESC default)
 - = 2 one and two-electron integrals (RESC default)

For RESC and OPRESC=1, NESOC=2 is not implemented, use NESOC=1 as the closest available possibility.

- NRATOM the number of different elements to be treated nonrelativistically. For example, in Pb3O4, to treat only lead relativistically, enter NRATOM=1. For NESC, this parameter affects the choice of the basis sets, you should use identical large, small, and averaged basis set for such atoms. For RESC, this parameter means that OPRESC=1 will not cause uncontracting primitives for such atoms.(default=0)

- CHARGE array containing charges of atoms to be treated nonrelativistically. (e.g. CHARGE(1)=8.0, to drop all oxygen atoms)

* * * the next parameters are used only with RELWFN=RESC:

- OMTTOL same as in \$CONTRL, but used for the preparation of the RI space for RESC. (default: from \$CONTRL).

- RESCTO tolerance for equating nearly degenerate eigenvalues of the kinetic energy and overlaps, which is used for evaluating RESC gradient. Values that are too large (>1e-6) can cause numerical errors in the gradient, approximately on the same order as RESCTO. Too small values can add very large values to the gradient due to division by numbers that are zero within machine precision that are not avoided with this tolerance filter. The recommended values for OPRESC=1 are 1e-6 for gold to 1e-7 for silver. For OPRESC=0, 1d-8 or smaller can be used.

\$EFIELD group (not required)

This group permits the study of the influence of an external electric field on the molecule. The method is general, and so works for all ab initio SCFTYPs.

- EVEC = an array of the three x,y,z components of the applied electric field, in a.u., where $1 \text{ Hartree/e}^* \text{ bohr} = 5.1422082(15) \text{ d+11 V/m}$
- SYM = a flag to specify when the field to be applied breaks the molecular symmetry. Since most fields break symmetry, the default is .FALSE.
-

Restrictions: analytic Hessians are not available, but numerical Hessians are. Because an external field causes a molecule with a dipole to experience a torque, geometry optimizations must be done in Cartesian coordinates only. Internal coordinates eliminate the rotational degrees of freedom, which are no longer free.

Notes: a Hessian calculation will have two rotational modes with non-zero "frequency", caused by the torque. A gas phase molecule will rotate so that the dipole moment is anti-parallel to the applied field. To carry out this rotation during geometry optimization will take many steps, and you can help save much time by inputting a field opposite the molecular dipole. There is also a stationary point at higher energy with the dipole parallel to the field, which will have two imaginary frequencies in the Hessian. Careful, these will appear as the first two modes in a Hessian run, but will not have the i for imaginary included on the printout since they are rotational modes.

For an application, see

H.Kono, S.Koseki, M.Shiota, Y.Fujimura *J.Phys.Chem.A* 105, 5627-5636(2001)

\$INTGRL group (optional)

This group controls AO integral formats. It should probably never be given, as the program always picks sensible values.

- SCHWRZ = a flag to activate use of the Schwarz inequality to predetermine small integrals. There is no loss of accuracy when choosing this option, and there are appreciable time savings for bigger molecules. Default=.TRUE. for over 5 atoms, or for direct SCF, and is .FALSE. otherwise.
- QFMM = a flag to use the quantum fast multipole method for linear scaling Fock matrix builds. This is available for RHF, UHF, and ROHF wavefunctions, and for DFT, but not with any other correlation treatment. You must select DIRSCF=.TRUE. In \$SCF if you use this option. The Optimal Parameter FMM code will run at a comparable speed to a ordinary run doing all integrals for molecules about 15 Angstroms in size, and should run faster for 20 Angstroms or more. See also the \$FMM group. (default=.FALSE.)

Various antiquated parameters follow:

- NOPK = 0 PK integral option on, which is permissible for RHF, UHF, ROHF, GVB energy/gradient runs.
 = 1 PK option off (default for all jobs). Must be off for anything with a transformation.
- NORDER = 0 (default)
 = 1 Sort integrals into canonical order. There is little point in selecting this option, as no part of GAMESS requires ordered integrals. See also NSQUAR.
- NINTMX = Maximum no. of integrals in a record block.
 (default=15000 for J or P file, =10000 for PK)

The following parameters control the integral sort.

- NSQUAR = 0 Sorted integrals will be in triangular canonical order (default)
 = 1 instead sort to square canonical order.
- NDAR = Number of direct access logical records to be used for the integral sort (default=2000)
- LDAR = Length of direct access records (site dependent)
- NBOXMX = 200 Maximum number of bins.
- NWORD = 0 Memory to be used (default=all of it).
- NOMEM = 0 If non-zero, force external sort.

The following parameters control integral restarts

- IST= 1 JST= 1 KST= 1 LST= 1
 NREC= 1 INTLOC= 1 (values given are defaults)

\$FMM group (relevant if QFMM selected in \$INTGRL)

This group controls the quantum fast multipole method evaluation of Fock matrices. The defaults are reasonable, so there is little need to give this input.

- ITGERR = Target error in final energy, to $10^{**}-(ITGERR)$ Hartree. The accuracy is usually better than the setting of ITGERR, in fact QFMM runs should suffer no loss of accuracy or be more accurate than a conventional integral run (default=7).
- QOPS = a flag to use the Quantum Optimum Parameter Searching technique, which finds an optimum FMM parameter set. (Default=.TRUE.)

If QOPS=.FALSE., the ITGERR value is not used. In this case the user should specify the following parameters:

- NP = the highest multipole order for FMM (Default=15).
- NS = the highest subdivision level (Default=2).
- IWS = the minimum well-separateness (Default=2).
- IDPGD = point charge approximation error ($10^{**}(-IDPGD)$) of the Gaussian products (Default=9).
- IEPS = very fast multipole method (vFMM) error, ($10^{**}(-IEPS)$) (Default=9)

\$TRANS group (optional for -CI- or -MCSCF-)
(relevant to analytic Hessians)
(relevant to energy localization)

This group controls the integral transformation. MP2 integral transformations are controlled instead by the \$MP2 input group. There is little reason to give any but the first variable.

- DIRTRF = a flag to recompute AO integrals rather than storing them on disk. The default is .FALSE. for MCSCF and CI runs. If your job reads \$SCF, and you select DIRSCF=.TRUE. in that group, a direct transformation will be done, no matter how DIRTRF is set.

Note that the transformation may do many passes over the AO integrals for large basis sets, and thus the direct recomputation of AO integrals can be very time consuming.

- MPTRAN = method to use for the integral transformation. the default is try 0, then 1, then 2.
- | | |
|---|---|
| 0 | means use the incore method |
| 1 | means use the segmented method. This is the only method that works in parallel. |
| 2 | means use the alternate method, which uses less memory than 2, but requires an extra large disk file. |
- NWORD = Number of words of fast memory to allow. Zero uses all available memory. (default=0)

CUTTRF = Threshold cutoff for keeping transformed two electron integrals.
(default= $10^{**}(-9)$)

AOINTS = defines AO integral storage during conventional integral transformations, during parallel runs.

DUP	stores duplicated AO lists on each node, and is the default for parallel computers with slow interprocessor communication, e.g. ethernet.
DIST	distributes the AO integral file across all nodes, and it is the default for parallel computers with high speed communications.

The remaining groups apply only to MCSCF and CI runs.

* * * * *

For hints on how to do MCSCF and CI
see the 'further information' section

* * * * *

\$CIINP group (optional, relevant for any CITYP)

This group is the control box for Graphical Unitary Group Approach (GUGA) CI calculations or determinant based CI. Each step which is executed potentially requires a further input group described later.

NRNFG = An array of 10 switches controlling which steps of a CI computation are performed. 1 means execute the module, 0 means don't.

NRNFG(1) = Generate the configurations. See either \$CIDRT or \$CIDET input. (default=1)

NRNFG(2) = Transform the integrals. See \$TRANS. (default=1)

NRNFG(3) = Sort integrals and calculate the Hamiltonian matrix. See \$CISORT and \$GUGEM. (default=1) This does not apply to determinants.

NRNFG(4) = Diagonalize the Hamiltonian matrix. See \$GUGDIA or \$CIDET. (default=1)

NRNFG(5) = Construct the one electron density matrix, and generate NO's. See \$GUGDM or \$CIDET. (default=1)

NRNFG(6) = Construct the two electron density matrix. See \$GUGDM2 or \$CIDET. (default=0 normally, but 1 for CI gradients)

NRNFG(7) = Construct the Lagrangian of the CI function. Requires DM2 matrix exists. See \$LAGRAN. (default=0 normally, but 1 for CI gradients) This does not apply to determinants.

NRNFG(8-10) are not used.

Users are not encouraged to change these values, as the defaults are quite reasonable ones.

NPFLG = An array of 10 switches to produce debug printout. There is a one to one correspondence to NRNFG, set to 1 for output. (default = 0,0,0,0,0,0,0,0,0,0) The most interesting is NPFLG(2)=1 to see the transformed 1e- integrals, NPFLG(2)=2 adds the very numerous transformed 2e- integrals to this.

IREST = n Restart the -CI- at stage NRNFG(n).

\$DET/\$GEN/\$CIDET/\$CIGEN

\$DET group (required for MCSCF if CISTEP=ALDET or ORMAS)
 \$GEN group (required for SCFTYP=MCSCF if CISTEP=GENCI)
 \$CIDET group (required if CITYP=ALDET, ORMAS, or FSOCI)
 \$CIGEN group (required if CITYP=GENCI)

This group describes the determinants to be used in a MCSCF or CI wavefunction:

a) For full CI calculations (ALDET) the \$DET/\$CIDET will generate a full list of determinants. If the CI is part of an MCSCF, this means the MCSCF is of the FORS type (which is also known as CASSCF).

b) For Occupation Restricted Multiple Active Space (ORMAS) CI, the input in \$ORMAS will partition the active orbitals defined here into separate spaces, that is, provide both \$DET/\$CIDET and \$ORMAS.

c) For Full Second Order CI, provide \$CIDET and \$SODET inputs.

d) For a general CI (meaning user specified space orbital products) provide \$DET/\$CIDET plus \$GEN/\$CIGEN and most likely \$GCILST (according to the keyword GLIST).

In the above, group names for MCSCF/CI jobs are separated by a slash.

Determinants contain several spin states, in contrast to configuration state functions. The Sz quantum number of each determinant is the same, but the Hamiltonian eigenvectors will have various spins $S=S_z, S_z+1, S_z+2, \dots$ so NSTATE may need to account for states of higher spin symmetry. In Abelian groups, you can specify the exact spatial symmetry you desire.

GLIST = general determinant list option
 The keyword GLIST must not be given in a \$DET or \$CIDET input group!
 These both generate full determinant lists, automatically.
 = INPUT means an input \$GCILST group will be read.
 = EXTRNL means the list will be read from a disk file GCILIST generated in an earlier run.
 = SACAS requests generation of several CAS spaces of different space symmetries, specified by the input IRREPS. This option is intended for state averaged calculations for cases of high symmetry, where degenerate irreps of the true group may fall into different irreps of the Abelian subgroup used.

* * * The next four define the orbital spaces * * *

There is no default for NCORE, NACT, and NELS:

NCORE = total number of orbitals doubly occupied in all determinants.

NACT = total number of active orbitals.

NELS = total number of active electrons.

SZ = azimuthal spin quantum number for each of the determinants, two times SZ is therefore the number of excess alpha spins in each determinant. The default is $SZ=S$, extracted from the $MULT=2S+1$ given in \$CONTRL.

* * * The following determine the state symmetry * * *

GROUP = name of the point group. The default is to copy this from \$DATA, if that group is Abelian (C2, Ci, Cs, C2v, C2h, D2, or D2h). If not, the group is set to C1 (no symmetry used).

ISTSYM = specifies the spatial symmetry of the state.
This table is exactly the same as in \$DRT input.

ISTSYM= 1 2 3 4 5 6 7 8

C1 A

Ci Ag Au

Cs A' A''

C2 A B

C2v A1 A2 B1 B2

C2h Ag Bu Bg Au

D2 A B1 B2 B3

D2h Ag B1g B2g B3g Au B1u B2u B3u

Default is ISTSYM=1, the totally symmetric state.

IRREPS = specifies the symmetries of the GLIST=SACAS space determinant list.
This variable should always be an array, as a single symmetry is more quickly obtained by the regular full CI code. The values given have the same meaning as the ISTSYM table.

* * * the following control the diagonalization * * *

NSTATE = Number of CI states to be found, the default is 1. The maximum number of states is 100.

PRTTOL = Printout tolerance for CI coefficients, the default is to print any larger than 0.05.

ANALYS = a flag to request analysis of the CI energy in terms of single and double excitation pair correlation energies. This is normally used in CI computations, rather than MCSCF, and when the wavefunction is dominated by a single reference, as the analysis is done in terms of excitations from the determinant with largest CI coefficient. The default is .FALSE.

ITERMX = Maximum number of Davidson iterations per root. The default is 100. A CI calculation will fail if convergence is not obtained before reaching the limit. MCSCF computations will not bomb if the iteration limit is reached, instead the last CI vector is used to proceed into the next orbital update. In cases with very large active spaces, it may be faster to input ITERMX=2 or 3 to allow the program to avoid fully converging the CI eigenvalue problem during the early MCSCF iterations. For small active spaces, it is best to allow the CI step to be fully converged on every iteration.

CVGTOL = Convergence criterion for Davidson eigenvector routine. This value is proportional to the accuracy of the coefficients of the eigenvectors found. The energy accuracy is proportional to its square. The default is 1.0E-5.

- NHGSS = dimension of the Hamiltonian submatrix which is diagonalized to obtain the initial guess eigenvectors. The determinants forming the submatrix are chosen on the basis of a low diagonal energy, or if needed to complete a spin eigenfunction. The default is 300.
- NSTGSS = Number of eigenvectors from the initial guess Hamiltonian to be included in the Davidson's iterative scheme. It is seldom necessary to include extra states to obtain convergence to the desired states. The default equals NSTATE.
- MXXPAN = Maximum number of expansion basis vectors in the iterative subspace during the Davidson iterations before the expansion basis is truncated. The default is the larger of 10 or 2*NSTGSS. Larger values might help convergence, do not decrease this parameter below 2*NSTGSS.
- CLOBBR = a flag to erase the disk file containing CI vectors from the previous MCSCF iteration. The default is to use these as starting values for the current iteration's CI. If you experience loss of spin symmetry in the CI step, reverse the default, to always take the CI from the top. Default = .FALSE.

* * * the following control the 1st order density * * *

These are ignored during MCSCF, but are used during a CI.

- IROOT = the root whose density is saved on the disk file for subsequent property analysis. Only one root can be saved, and the default value of 1 means the ground state. Be sure to set NFLGDM to form the density of the state you are interested in!
- NFLGDM = Controls each state's density formation.
 0 do not form density for this state.
 1 form density and natural orbitals for this state, print and punch occ.num. and NOs.
 2 same as 1, plus print density over MOs.
 The default is NFLGDM(1)=1,0,0,...,0 meaning only ground state NOs are generated.

* * * the following control the state averaged

* * * 1st and 2nd order density matrix computation

Usually ignored by CI runs, these are relevant to MCSCF.

- PURES = a flag controlling the spin purity of the state averaging. If true, the WSTATE array pertains to the lowest states of the same S value as is given by the MULT keyword in \$CONTRL. In this case the value of NSTATE will need to be bigger than the total number of weights given by WSTATE if there are other spin states present at low energies. If false, it is possible to state average over more than one S value, which might be of interest in spin-orbit coupling jobs. The default is .TRUE.
- WSTATE = An array of up to 100 weights to be given to the densities of each state in forming the average. The default is to optimize a pure ground state, WSTATE(1)=1.0,0.0,...,0.0 A small amount of the ground state can help

the convergence of excited states greatly. Gradient runs are possible only with pure states. Be sure to set NSTATE above appropriately!

\$ORMAS group (required for SCFTYP=MCSCF if CISTEP=ORMAS)
(required for CITYP=ORMAS)

This group partitions an active space, defined in \$DET or \$CIDET, into Occupation Restricted Multiple Active Spaces (ORMAS). All possible determinants satisfying the occupation restrictions (and of course the space symmetry restriction given in \$DET/\$CIDET) will be generated. This group's usefulness lies in reducing the large number of determinants present in full CI calculations with large active spaces.

There are no sensible defaults for these inputs, but if the group is entirely omitted, a full CI calculation will be performed. That is, the defaults are

NSPACE=1, MSTART(1)=NCORE+1, MINE(1)=NELS, MAXE(1)=NELS
meaning all active orbitals are in one partition.

NSPACE = number of orbital groups you wish to partition the active space (NACT in \$DET/\$CIDET) into.

MSTART = an array of NSPACE integers. These specify where each orbital group starts in the full list. You must not overlook the NCORE core orbitals in computing MSTART values. Space I runs from orbital MSTART(I) up to orbital MSTART(I+1)-1, or NACT+NCORE if I is the last space, I=NSPACE.

IMPORTANT !!!! Remember to make sure your orbitals have been reordered to suit MSTART, using NORDER in \$GUESS.

MINE = an array of NSPACE integers. These specify the minimum numbers of electrons that must always occupy the orbital groups. In other words, MINE(I) is the minimum number of electrons that can occupy space I in any of the determinants.

MAXE = an array of NSPACE integers. These specify the maximum numbers of electrons that must always occupy the orbital groups. In other words, MAXE(I) is the maximum number of electrons that can occupy space I in any of the determinants.

The number of active electrons is NELS in \$DET or \$CIDET, and the program will check that MINE/MAXE values are consistent with this total number.

*** See REFS.DOC for more information on using ORMAS ***

\$GCILST group (required for SCFTYP=MCSCF if CISTEP=GENCI)
(required if CITYP=GENCI)

This group defines space products to be used in the general CI calculation, or in a MCSCF wavefunction. The input is free format.

Line 1: NSPACE ISYM

The first line gives the total number of space products to be entered in the second lines. The option ISYM can be omitted, or given as 0, in which case the program will verify that all space products typed in the second lines indeed have the spatial symmetry defined by ISTSYM in the \$GEN or \$CIGEN input groups. If ISYM is 1, the user is indicating that more than one space symmetry is known to be in the list, that this is intentional, and the program should proceed with the calculation. This might be of use in state averaging two representations in a group that has more than two total representations, and therefore faster than turning symmetry off completely by GROUP=C1. ISYM=2 has the same meaning but turns on additional printing.

Line 2 is repeated NSPACE times. Each line 2 contains NACT integers, which must be 0, 1, or 2, and therefore tells the occupation of each of the active orbitals in each space product. An example input is:

```
$GEN GLIST=INPUT NELS=6 NACT=4 SZ=0.0 $END
$GCILST
5
2 2 2 0
2 1 2 1
2 0 2 2
2 2 0 2
0 2 2 2
$END
```

which generates 6 Ms=0 determinants, much less than the 16 determinants in a C1 symmetry full list for 6 e- in 4 MOs.

The second space product above generates two determinants. All space products with singly occupied orbitals are used to form all possible determinants, to ensure that the final states are eigenfunctions of the S^2 operator (meaning they will be pure spin states).

Note that there is no way at present to generate lists such as singles and doubles from a single reference.

Convergence of MCSCF calculations will depend on how well chosen your determinant list is, and may very well require the use of the FULLNR or JACOBI convergers.

\$SODET group (required if CITYP=FSOCI)

This group controls a full second order CI calculation using determinants (see also the keyword SOCI in \$CIDRT). Most of the characteristics of the active space (such as NCORE, NACT, NELs) must be given in a \$CIDET group, as a preliminary full CI according to \$CIDET will be made. The FCI states will then be used as the initial guess for the full second order CI. A few additional parameters may be given in this group, but many runs will not need to give any of these.

- NEXT = the number of external orbitals to be included.
The default is the entire virtual MO space.
- NSOST = the number of states to be found in the SOCI.
The default is copied from NSTATE in \$CIDET.
- MAXPSO = maximum expansion space size used in the SOCI.
The default is copied from MXXPAN in \$CIDET.
- ORBS = MOS means use the MCSCF orbitals, which should be allowed to undergo canonicalization (see the CANONC keyword in \$MCSCF), or the input \$VEC group in case SCFTYP=NONE. (default)
NOS means to instead use the natural orbitals of the MCSCF.

\$DRT group (required for SCFTYP=MCSCF if CISTEP=GUGA)
 \$CIDRT group (required for CITYP=GUGA)

This group describes the -MCSCF- or -CI- wavefunction. The distinct row table is the means by which the Graphical Unitary Group Approach (GUGA) names the configurations.

The group is spelled DRT for MCSCF runs, and CIDRT for CI runs. The main difference in these is NMCC vs. NFZC.

There is no default for GROUP, and you must choose one of FORS, FOCI, SOCI, or IEXCIT.

- GROUP = the name of the point group to be used. This is usually the same as that in \$DATA, except for RUNTYP=HESSIAN, when it must be C1. Choose from the following: C1, C2, CI, CS, C2V, C2H, D2, D2H, C4V, D4, D4H. If your \$DATA group is not listed, choose only C1 here.
- FORS = flag specifying the Full Optimized Reaction Space set of configuration should be generated. This is usually set true for MCSCF runs, but if it is not, see FORS in \$MCSCF. Default=.FALSE.
- FOCI = flag specifying first order CI. In addition to the FORS configurations, all singly excited CSFs from the FORS reference are included. Default=.FALSE.
- SOCI = flag specifying second order CI. In addition to the FORS configurations, all singly and doubly excited configurations from the FORS reference are included. Default=.FALSE.
- IEXCIT = electron excitation level, for example 2 will lead to a singles and doubles CI. This variable is computed by the program if , FOCI, or SOCI is chosen, otherwise it must be entered.
- INTACT = flag to select the interacting space option. See C.F.Bender, H.F.Schaefer J.Chem.Phys. 55, 4798-4803(1971). The CI will include only those CSFs which have non-vanishing spin couplings with the reference configuration. Note that when the Schaefer group uses this option for high spin ROHF references, they use Guest/Saunders orbital canonicalization.

* * the next variables define the single reference * *

The single configuration reference is defined by filling in the orbitals by each type, in the order shown. The default for each type is 0.

- Core orbitals, which are always doubly occupied:
- NMCC = number of MCSCF core MOs (in \$DRT only).
 NFZC = number of CI frozen core MOs (in \$CIDRT only).

Internal orbitals, which are partially occupied:

NDOC = number of doubly occupied MOs in the reference.

NAOS = number of alpha occupied MOs in the reference, which are singlet coupled with a corresponding number of NBOS orbitals.

NBOS = number of beta spin singly occupied MOs.

NALP = number of alpha spin singly occupied MOs in the reference, which are coupled high spin.

NVAL = number of empty MOs in the reference.

External orbitals, occupied only in FOCI or SOCI:

NEXT = number of external MOs. If given as -1, this will be set to all remaining orbitals (apart from any frozen virtual orbitals).

NFZV = number of frozen virtual MOs, never occupied.

* * the next two help with state symmetry * *

ISTSYM = irreducible representation for GUGA wavefunction. This option overwrites whatever symmetry is implied by NALP/NAOS/NBOS. Default=0 means ISTSYM will be inferred from the symmetry of the reference, namely from the symmetry of NALP/NAOS/NBOS orbitals.

ISTSYM=	1	2	3	4	5	6	7	8
C1	A							
Ci	Ag	Au						
Cs	A'	A''						
C2	A	B						
C2v	A1	A2	B1	B2				
C2h	Ag	Bu	Bg	Au				
D2	A	B1	B2	B3				
D2h	Ag	B1g	B2g	B3g	Au	B1u	B2u	B3u

It is no doubt easier to just select the desired ISTSYM directly. Its computation from the singly occupied orbitals is kept merely to preserve old input files.

NOIRR = controls labelling of the CI state symmetries.

= 1 no labelling (default)

= 0 usual labelling. This can be very time consuming if the group is non-Abelian.

= -1 fast labelling, in which all CSFs with small CI coefficients are ignored. This can produce weights quite different from one, due to ignoring the small coefficients, but overall seems to work OK. Note that it is normal for the weights not to sum to 1 even for NOIRR=0 because for simplicity the weight determination is focused on the relative weights rather than absolute. However weight do not sum to one only for row-mixed MOs.

= -2,-3... fast labelling and sets SYMTOL=10**NOIRR for runs other than TRANSITN. All irreps with weights greater than SYMTOL are considered.

* * * the final choices are seldom used * * *

MXNINT = Buffer size for sorted integrals. (Default=20000)
Adjust this upwards if the program tells you to, which may occur in cases with large numbers of external orbitals.

MXNEME = Buffer size for energy matrix. (default=10000)

NPRT = Configuration printout control switch.

This can consume a HUMUNGUS amount of paper!

- 0 no print (default)
- 1 print electron occupancies, one per line.
- 2 print determinants in each CSF.
- 3 print determinants in each CSF (for Ms=S-1).

\$MCSCF group (optional for -MCSCF-)

This group controls the MCSCF orbital optimization step. The difference between the five convergence methods is outlined in Chapter Four of this manual, which you must carefully study before attempting MCSCF computations.

--- the next chooses the configuration basis ---

- CISTEP = ALDET chooses the Ames Lab. determinant full CI, and requires \$DET input. (Default)
- = ORMAS chooses an Occupation Restricted Multiple Active Space determinant CI, requiring both \$DET and \$ORMAS inputs.
- = GUGA chooses the graphical unitary group CSFs, and requires \$DRT input. This is the only value usable with the QUAD converger.
- = GENCI chooses the Ames Lab. general CI, and requires \$GEN input.

ive choose the orbital optimizer ---

- FOCAS = a flag to select a method with a first order convergence rate. (default=.FALSE.)
Parallel runs with FOCAS do not use MEMDDI.
- SOSCF = a flag selecting an approximately second order convergence method, using an approximate orbital hessian. (default=.TRUE.)
Parallel runs with SOSCF do not use MEMDDI.
- FULLNR = a flag selecting a second order method, with an exact orbital hessian. (default=.FALSE.)
Parallel runs with FULLNR require input of MEMDDI.
- QUAD = a flag to pick a fully quadratic (orbital and CI coefficient) optimization method, which is applicable to FORS or non-FORS wavefunctions. QUAD may not be used with state-averaging. (default = .FALSE.)
This converger can be used only in serial runs.
- JACOBI = a flag to pick a program that minimizes the MCSCF energy by a sequence of 2x2 Jacobi orbital rotations. This is very systematic in forcing convergence, although the number of iterations may be high and the time longer than the other procedures. This option does not compute the orbital Lagrangian, hence at present nuclear gradients may not be computed. (default = .FALSE.)
This converger can be used only in serial runs.

Note that FOCAS must be used only with FORS=.TRUE. in \$DRT. The other convergers are usable for either FORS or non-FORS wavefunctions, although convergence is always harder in the latter case, when FORS below must be set .FALSE.

--- the next apply to all convergence methods ---

- FORS = a flag to specify that the MCSCF function is of the Full Optimized Reaction Space type, which is sometimes known as CAS-SCF. .TRUE. means omit active-active rotations from the optimization. Since convergence is usually better with these rotations included, the default is sensible:

.TRUE. for FOCAS, .FALSE. for FULLNR or QUAD, and for SOSCF, .TRUE. for ALDET/GUGA but .FALSE. for ORMAS/GENCI)

- ACURCY = the major convergence criterion, the maximum permissible asymmetry in the Lagrangian matrix. (default=1.0E-05)
- ENGTOl = a secondary convergence criterion, the run is considered converged when the energy change is smaller than this value. (default=1.0E-10)
- MAXIT = Maximum number of iterations (default=100 for FOCAS, 60 for SOSCF, 30 for FULLNR or QUAD)
- MICIT = Maximum number of microiterations within a single MCSCF iteration. (default=5 for FOCAS or SOSCF, or 1 for FULLNR or QUAD)
- NWORD = The maximum memory to be used, the default is to use all available memory. (default=0)
- CANONC = a flag to cause formation of the closed shell Fock operator, and generation of canonical core orbitals. This will order the MCC core by their orbital energies. (default=.TRUE.)
- EKT = a flag to cause generation of extended Koopmans' theorem orbitals and energies. (Default=.FALSE.)
For this option, see R.C.Morrison and G.Liu, J.Comput.Chem., 13, 1004-1010 (1992). Note that the process generates non-orthogonal orbitals, as well as physically unrealistic energies for the weakly occupied MCSCF orbitals. The method is meant to produce a good value for the first I.P.
- NPUNCH = MCSCF punch option (analogous to \$SCF NPUNCH)
= 0 do not punch out the final orbitals
= 1 punch out the occupied orbitals
= 2 punch out occupied and virtual orbitals
The default is NPUNCH = 2.
- NPFLG = an array of debug print control. This is analagous to the same variable in \$CIINP. Elements 1,2,3,4,6,8 make sense, the latter controls debugging the orbital optimization.

--- the next refers to SOSCF optimizations ---

- NOFO = set to 1 to skip use of FOCAS for one iteration during SOSCF. This is a testing parameter, at present NOFO defaults to 0 to do one FOCAS iter.

--- the next three refer to FOCAS optimizations ---

- CASDII = threshold to start DIIS (default=0.05)
- CASHFT = level shift value (default=1.0)
- NRMCAS = renormalization flag, 1 means do Fock matrix renormalization, 0 skips (default=1)

--- the next applies to the QUAD method ---
 (note that all FULLNR input is also relevant to QUAD)

QUDTHR = threshold on the orbital rotation parameter, SQCDF, to switch from the initial FULLNR iterations to the fully quadratic method. (default = 0.05)

--- The JACOBI converger accepts FULLNR options ---
 --- NORB, NOROT, MOFRZ, and FCORE as input ---

--- all remaining input applies only to FULLNR ---

DAMP = damping factor, this is adjusted by the program as necessary.
 (default=0.0)

METHOD = DM2 DM2 selects a density driven construction of the Newton-Raphson matrices. (default).
 = TEI selects 2e- integral driven NR construction.
 See the 'further information' section for more details concerning these methods. TEI is slow!

LINSER = a flag to activate a method similar to direct minimization of SCF. The method is used if the energy rises between iterations. It may in some circumstances increase the chance of converging excited states.
 (default=.FALSE.)

FCORE = a flag to freeze optimization of the MCC core orbitals, which is useful in preparation for RUNTYP=TRANSITN jobs. Setting this flag will automatically force CANONC false. This option is incompatible with gradients, so can only be used with RUNTYP=ENERGY. It is a good idea to decrease TOLZ and TOLE in \$GUESS by two orders of magnitude to ensure the core orbitals are unchanged during input. (default=.FALSE.)

--- the last four FULLNR options are seldom used ---

DROPC = a flag to include MCC core orbitals during the CI computation. The default is to drop them during the CI, instead forming Fock operators which are used to build the correct terms in the orbital hessian. (default = .TRUE.)

NORB = the number of orbitals to be included in the optimization, the default is to optimize with respect to the entire basis. This option is incompatible with gradients, so can only be used with RUNTYP=ENERGY.
 (default=number of AOs given in \$DATA).

MOFRZ = an array of orbitals to be frozen out of the orbital optimization step
 (default=none frozen).

NOROT = an array of up to 250 pairs of orbital rotations to be omitted from the NR optimization process. The program automatically deletes all core-core rotations, all act-act rotations if FORS=.T., and all core-act and core-virt rotations if FCORE=.T. Additional rotations are input as I1,J1,I2,J2... to exclude rotations between orbital I running from 1 to

NORB, and J running up to the smaller of I or NVAL in \$TRANS.

\$MCQDPT group (relevant to SCFTYP=MCSCF if MPLEVL=2)

Controls 2nd order MCQDPT (multiconfiguration quasi- degenerate perturbation theory) runs, if requested by MPLEVL=2 in \$CONTRL. MCQDPT2 is implemented only for FORS (aka CASSCF) wavefunctions. The MCQDPT method is a multistate, as well as multireference perturbation theory. The implementation is a separate program, interfaced to GAMESS, with its own procedures for determination of the canonical MOs, CSF generation, integral transformation, CI in the reference CAS, etc. Therefore some of the input in this group repeats data given elsewhere, particularly the \$DET/\$DRT.

Analytic gradients are not available. Spin-orbit coupling may be treated as a perturbation, included at the same time as the energy perturbation. If spin- orbit calculations are performed, the input groups for each multiplicity are named \$MCQD1, \$MCQD2, ... Rather than \$MCQDPT. Parallel calculation is implemented.

When applied to only one state, the theory is known as multi-reference Moller-Plesset (MRMP), so the term MCQDPT is more appropriate when this theory is used in its multi- state form. Please note that this perturbation theory is not the same thing as the CASPT2 theory, and should -NEVER- be called that. A more complete discussion may be found in the 'Further Information' chapter.

*** MCSCF reference wavefunction ***

NEL = total number of electrons, including core. (default from \$DATA and ICHARG in \$CONTRL)
 MULT = spin multiplicity (default from \$CONTRL)
 NMOACT = Number of orbitals in FORS active space (default is the active space in \$DET or \$DRT)
 NMOFZC = number of frozen core orbitals, NOT correlated in the perturbation calculation. (default is number of chemical cores)
 NMODOC = number of orbitals which are doubly occupied in every MCSCF configuration, that is, not active orbitals, which are to be included in the perturbation calculation. (The default is all valence orbitals between the chemical core and the active space)
 NMOFZV = number of frozen virtuals, NOT occupied during the perturbation calculation. The default is to use all virtuals in the MP2. (Default=0)

If the input file does not provide a \$DET or \$DRT, the user must give NMOFZC, NMODOC, and NMOACT correctly here.

ISTSYM = the state symmetry of the target state(s).
 This is given as an integer, note that only Abelian groups in \$DATA are supported:

ISTSYM=	1	2	3	4	5	6	7	8
C1	A							
Ci	Ag	Au						
Cs	A'	A''						
C2	A	B						
C2v	A1	A2	B1	B2				
C2h	Ag	Bu	Bg	Au				
D2	A	B1	B2	B3				
D2h	Ag	B1g	B2g	B3g	Au	B1u	B2u	B3u

(The default is inherited from \$DET or \$DRT)

NOSYM = 0 use CSF symmetry (see the ISTSYM keyword). off diagonal perturbations vanish if states are of different symmetry, so the most efficient computation is a separate run for every space symmetry. (default)
 1 turn off CSF state symmetry so that all states are treated at once. ISTSYM is ignored. Presently this option does not seem to work!!
 -1 Symmetry purify the orbitals. Since \$GUESS is not read by MCQDPT runs, this option can be used as a substitute for its PURIFY. After cleaning the orbitals, they are reorthogonalised within each irrep and within each group (core, double, active, virtual) separately. Since this occurs after MCSCF optimization (see INORB), it is *your* responsibility to verify that the changes made to the orbitals are small enough that the CAS energies for the original CASSCF and the CAS-CI performed during MCQDPT give the same energies!

*** perturbation specification ***

KSTATE = state is used (1) or not (0) in the MCQDPT2. Maximum of 20 elements, including zeros. For example, if you want the perturbation correction to the second and the fourth roots, KSTATE(1)=0,1,0,1 See also WSTATE. (default=1,0,0,0,0,0,0,...)

*** MO input and flow control ***

INORB = 0 optimize the MCSCF wavefunction in this run.
 = 1 read the converged orbitals from a \$VEC group, and skip immediately to the MCQDPT computation. A complete \$VEC including virtuals must be given. (Default=0)

*** Intruder State Removal ***

EDSHFT = energy denominator shifts. (default=0.0,0.0) Intruder State Free (ISF, aka ISA) calculations can be made by changing the energy denominators around poles (where the denominator is zero). Each denominator x is replaced by $x + \text{EDSHFT}/x$, so that far from the poles (when x is large) the effect of such change is small. EDSHFT is an array of two values, the first is used in spin-free MCQDPT, and the second is for spin-orbit MCQDPT. Both values are used if RUNTYP=TRNSTN, only the first is used otherwise. A suggested pair of values is 0.02,0.1, but experimentation with your system is recommended. Setting these values to zero is ordinary MCQDPT, and infinite collapses to the MCSCF reference. Note that the energy denominators (which are ket-dependent in MCQDPT) are changed in a different way for each ket-vector, that is, for each row in MCQDPT Hamiltonian matrix. In other words, the zeroth order energies are not "universal", but state specific. This is strictly speaking some weak inconsistency in defining zeroth order energies that are usually chosen "universally".

In order to maintain continuity when studying a PES, one usually uses the

same EDSHFT values for all points on PES. In order to study the potential surface for any extended range of geometries, it is recommended to use ISF, as it is quite likely that one or more regions of the PES will be unphysical due to intruder states.

For an example of how intruder states can appear at some points on the PES, see Figures 1,2,7 of

K.R.Glaesemann, M.S.Gordon, H.Nakano Phys.Chem.Chem.Phys. 1, 967-975(1999)

For a discussion of intruder state removal from MCQDPT, see

Y.-K.Choe, H.A.Witek, J.P.Finley, K.Hirao J.Chem.Phys. 114, 3913-3918(2001)

Note that the formula given above corresponds to the choice of equation 23 in this paper, with

$$\text{delta-q} = \text{EDSHIFT}/\text{delta-E-naught-alpha,q}$$

rather than equation 20. For an application, see

H.A.Witek, D.G.Fedorov, K.Hirao, A.Viel, P.-O.Widmark J.Chem.Phys. 116, 8396-406(2002)

See also REFWGT.

REFWGT = a flag to request decomposition of the second order energy into internal, semi-internal, and external contributions, and to obtain the weight of the MCSCF reference in the 1st order wave function. This option significantly increases the run time! When you run in parallel, only the transformation steps will speed up, as the PT part of the reference weight calculation has not been adapted for speedups (default = .FALSE.)

The EDSHFT option does not apply if REFWGT is used. One purpose of using REFWGT is to try to understand the nature of the intruder states.

*** Canonical Fock orbitals ***

IFORB = 0 omit this step.
 = 1 determine the canonical Fock orbitals. (default)
 = 3 canonicalise the Fock orbitals averaged over all \$MCQDx input groups. This option pertains only to RUNTYP=TRANSITN. It is primarily meant to include spin-orbit coupling perturbation into the energy perturbation, but could also be used in conjunction with OPERAT=DM to calculate only the second order energy perturbation. IFORB=3 means that WSTATE is used as follows: In each \$MCQDx group, the WSTATE weights are divided by the total number of states (sum(i) IROOTS(i)), so the sum over all WSTATE values in all \$MCQDx groups is normalized to sum to 1. Thus there is no normalisation to 1 within each \$MCQDx group. This option might be used to speed up an atomic MCQDPT, e.g. if computing the 3-P ground state of carbon, one would want to average over all three spatial components of the P term, to be sure of spatial degeneracy, but then run the perturbation using symmetry, separately on the B1g+B2g+B3g subspecies (within D2h) of a P term. It is very important to give weights, appropriate for the symmetry, the input requires care.

WSTATE = weight of each CAS-CI state in computing the closed shell Fock matrix. You must enter 0.0 whenever the same element in KSTATE is 0. In most cases setting all WSTATE for states to be included in the MCQDPT to an equal value is the best. (default is WSTATE(1)=1.0,0.0,0.0,...)

*** Miscellaneous options ***

ISELCT is an option to select only the important CSFs for inclusion into the CAS-CI reference states. Set to 1 to select, or to 0 to avoid selection of CSFs (default = 0) All CSFs in a preliminary complete active space CI whose CI coefficients exceed the square root of THRWGT are kept in a smaller CI to determine the zero-th order states. Note that the CSFs with smaller coefficients, while excluded from the reference states, are still used during the perturbation calculation, so most of their energy contribution is still retained. This can save appreciable computer time in cases with large active spaces.

THRWGT = weight threshold for retaining CSFs in selected configuration runs. In quantum mechanics, the weight of a CSF is the square of its CI coefficient. (default=1d-6)

THRGEN = threshold for one-, two-, and three-body density matrix elements in the perturbation calculation. The default gives about 6 decimal place accuracy in the energies. Increase to 1D-9 or 1D-10 if you wish to obtain higher accuracy (default=1D-8)

THRENE = threshold for the energy convergence in the Davidson's method CAS-CI. (default=-1.0D+00)

THRCON = threshold for the vector convergence in the Davidson's method CAS-CI. (default=1.0D-06)

MDI = dimension of small Hamiltonian diagonalized to prepare initial guess CI states. (default=50)

MXBASE = maximum number of expansion vectors in the Davidson diagonalization subspace (e.g. MXXPAN). (default=50)

NSOLUT = number of states to be solved for in the Davidson's method, this might need to exceed the number of states in the perturbation treatment in order to "capture" the correct roots.

NSTOP = maximum number of iterations to permit in the Davidson's diagonalization.

LPOUT = print option, 0 gives normal printout, while <0 gives debug print (e.g. -1,-5,-10,-100). In particular, LPOUT=-1 gives more detailed timing information. (Default=0)

The next three parameters refer to parallel execution:

DOORDO = a flag to select reordering of AO integrals which speeds the integral transformations. This reduces disk writes, but increases disk reads, so you can try turning it off if your machine has slow writes.

(default=.TRUE.)

PARAIO = access 2e- integral file on every node, at the same time. This affects only runs with DOORDO true, and it may be useful to turn this off in the case of SMP nodes sharing a common disk drive. (default=.TRUE.)

DELSCR = a flag to delete file 56 containing half- transformed integrals after it has been used. This reduces total disk requirements if this file is big. (default=.FALSE.)

Note that parallel execution will be more effective if you use distributed memory, MEMDDI in \$SYSTEM. Use of AOINTS=DIST in \$TRANS is likely to be helpful in situations with relatively poor I/O rates compared to communication, e.g. SMP enclosures forced to share a single scratch disk system. See PROG.DOC for more information on parallel execution.

Finally, there are additional very specialized input options, described in the source code routine MQREAD:

IROT, LENGTH, MAXCSF, MAXERI, MAXROW, MXTRFR, THRERI, MAINCS,
NSTATE

\$CISORT group (optional, relevant for -CI- and -MCSCF-)

This group provides further control over the sorting of the transformed integrals.

- NDAR = Number of direct access records. (default = 2000)
- LDAR = Length of direct access record (site dependent)
- NBOXMX = Maximum number of boxes in the sort. (default = 200)
- NWORD = Number of words of fast memory to use in this step. A value of 0 results in automatic use of all available memory. (default = 0)
- NOMEM = 0 (set to one to force out of memory algorithm)
-

\$GUGEM group (optional, relevant for -CI- or -MCSCF-)

This group provides further control over the calculation of the energy (Hamiltonian) matrix.

- CUTOFF = Cutoff criterion for the energy matrix. (default=1.0E-8)
- NWORD = not used.
-

\$GUGDIA group (optional, relevant for -CI- or -MCSCF-)

This group provides control over the Davidson method diagonalization step.

- NSTATE = Number of CI states to be found. (default=1) You can solve for any number of states, but only 100 can be saved for subsequent sections, such as state averaging.
- PRTTOL = Printout tolerance for CI coefficients (default = 0.05)
- MXXPAN = Maximum no. of expansion basis vectors used before the expansion basis is truncated. (default=30)
- ITERMX = Maximum number of iterations (default=50)
- CVGTOL = Convergence criterion for Davidson eigenvector routine. This value is proportional to the accuracy of the coefficients of the eigenvector(s) found. The energy accuracy is proportional to its square. (default = 1.0E-5)
- NWORD = Number of words of fast memory to use in this step. A value of zero results in the use of all available memory. (default = 0)

\$GUGDIA/\$GUGDM

- MAXHAM = specifies dimension of Hamiltonian to try to store in memory. The default is to use all remaining memory to store this matrix in memory, if it fits, to reduce disk I/O to a minimum.
- MAXDIA = maximum dimension of Hamiltonian to send to an incore diagonalization. If the number of CSFs is bigger than MAXDIA, an iterative Davidson procedure is invoked. Default=100
- NIMPRV = Maximum no. of eigenvectors to be improved every iteration. (default = nstate)
- NSELECT = Determines initial guess to eigenvectors.
 = 0 Unit vectors corresponding to the NSTATE lowest diagonal elements and any diagonal elements within SELTHR of them. (default)
 < 0 First abs(NSELECT) unit vectors.
 > 0 use NSELECT unit vectors corresponding to the NSELECT lowest diagonal elements.
- SELTHR = Guess selection threshold when NSELECT=0. (default=0.01)
- NEXTRA = Number of extra expansion basis vectors to be included on the first iteration. NEXTRA is decremented by one each iteration. This may be useful in "capturing" vectors for higher states. (Default=5)
 On AXP processors, enter as 0 to avoid core dumps.
- KPRINT = Print flag bit vector used when NPFLG(4)=1 in the \$CIINP group (default=8)
 1 bit 0 print final eigenvalues
 2 bit 1 print final tolerances
 4 bit 2 print eigenvalues and tolerances at each truncation
 8 bit 3 print eigenvalues every iteration
 16 bit 4 print tolerances every iteration

Inputs for a multireference Davidson correction, in case the orbitals are from a MCSCF.

- NREF = number of CSFs in the MCSCF (full CI) job.
- EREF = the energy of the MCSCF reference.

\$GUGDM group (optional, relevant for -CI-)

This group provides further control over formation of the one electron density matrix. See NSTATE in \$GUGDIA.

- NFLGDM = Controls each state's density formation.
 0 do not form density for this state.
 1 form density and natural orbitals for this state, print and punch occ.num. and NOs.
 2 same as 1, plus print density over MOs. (default=1,99*0, means ground state NOs only)

Note that forming the 1-particle density for a state is negligible against the diagonalization time for that state.

- IROOT = The -CI- root whose density matrix is saved on the direct access dictionary file for later computation of properties. You may save only one state's density for property evaluation. (default=1)
- WSTATE = An array of up to 100 weights to be given to the 1 body density of each state in forming the DM1. It is not physically reasonable to average over any CI states that are not degenerate, but it may be useful to use WSTATE to produce a totally symmetric density when the states are degenerate. The averaged density will be used for property computations, as well as to generate natural orbitals. The default is to use NFLGDM/IROOT, unless WSTATE information is given, in which case NFLGDM/IROOT are ignored.
- IBLOCK = Density blocking switch. If nonzero, the off diagonal block of the density above row IBLOCK will be set to zero before the (approximate) natural orbitals are found. One use for this is to keep the internal and external orbitals in a FOCI or SOCI calculation from mixing, in which case IBLOCK is the highest occupied internal orbital. (default=0)
- NWORD = Number of words of memory to use. Zero means use all available memory (default=0).

\$GUGDM2 group (optional, relevant for -CI- or -MCSCF-)

This group provides control over formation of the 2-particle density matrix.

- WSTATE = An array of up to 100 weights to be given to the 2 body density of each state in forming the DM2. The default is to optimize a pure ground state. (Default=1.0,99*0.0) A small amount of the ground state can help the convergence of excited states greatly. Gradient runs are possible only with pure states.

Be sure to set NSTATE in \$GUGDIA appropriately!

- CUTOFF = Cutoff criterion for the 2nd-order density. (default = 1.0E-9)
- NWORD = Number of words of fast memory to use in sorting the DM2. The default uses all available memory. (default=0).
- NOMEM = 0 uses in memory sort, if possible.
= 1 forces out of memory sort.
- NDAR = Number of direct access records. (default=4000)
- LDAR = Length of direct access record (site dependent)
- NBOXMX = Maximum no. of boxes in the sort. (default=200)

\$LAGRAN group (optional, relevant for -CI- gradient)

This group provides further control over formation of the CI Lagrangian, a quantity which is necessary for the computation of CI gradients.

NOMEM = 0 form in core, if possible
 = 1 forces out of core formation
 NWORD = 0 (0=use all available memory)
 NDAR = 4000
 LDAR = Length of each direct access record (default is NINTMX from \$INTGRL)

\$TRFDM2 group (optional, relevant for -CI- gradient)

This group provides further control over the back transformation of the 2 body density to the AO basis.

NOMEM = 0 transform and sort in core, if possible
 = 1 transform in core, sort out of core, if poss.
 = 2 transform out of core, sort out of core
 NWORD = 0 (0=use all available memory)
 CUTOFF = 1.0D-9, threshold for saving DM2 values
 NDAR = 2000
 LDAR = Length of each direct access record (default is system dependent)
 NBOXMX = 200

Usually neither of these two groups is given. Since these groups are normally used only for CI gradient runs, we list here some of the restrictions on the CI gradients:

- a) SCFTYP=RHF, only
- b) no FZV orbitals in \$CIDRT, all MOs must be used.
- c) the derivative integrals are computed in the 2nd derivative code, which is limited to spd basis sets.
- d) the code does not run in parallel.
- e) Use WSTATE in \$GUGDM2 to specify the state whose gradient is to be found. Use IROOT in \$GUGDM to specify the state whose other properties will be found. These must be the same state!
- f) excited states often have different symmetry than the ground state, so think about GROUP in \$CIDRT.
- g) the gradient can probably be found for any CI for which you have sufficient disk to do the CI itself. Time is probably about 2/3 additional.

\$TRANST group (relevant for RUNTYP=TRANSITN)
(only for CITYP=GUGA or MPLEVL=2)

This group controls the evaluation of the radiative transition moment, or spin orbit coupling (SOC). An SOC calculation can be based on variational CI wavefunctions, using GUGA CSFs, or based on 2nd order perturbation theory using the MCQDPT multireference perturbation theory. These are termed SO-CI and SO-MCQDPT below. The orbitals are typically obtained by MCSCF computations, and since the CI or MCQDPT wavefunctions are based on those MCSCF states, the zero-th order states are referred to below as the CAS-CI states. SOC jobs prepare a model Hamiltonian mixed states, which are linear combinations of the CAS-CI states. If scalar relativistic corrections were included in the underlying spin-free wavefunctions, it is possible either to include or to neglect similar corrections to the spin-orbit integrals, see keyword NESOC in \$RELWFN.

An input file to perform SO-CI will contain

SCFTYP=NONE CITYP=GUGA MPLEVL=0 RUNTYP=TRANSITN

while a SO-MCQDPT calculation will have

SCFTYP=NONE CITYP=NONE MPLEVL=2 RUNTYP=TRANSITN

The SOC job will compute a Hamiltonian matrix as the sum of spin-free terms and spin-orbit terms, $H = H\text{-sf} + H\text{-so}$. For SO-CI, the matrix $H\text{-sf}$ is diagonal in the CAS-CI state basis, with the LS-coupled CAS-CI energies as the diagonal elements, and $H\text{-so}$ contains only off-diagonal couplings between these LS states,

$H\text{-sf} = \text{CAS-CI spin-free } E$

$H\text{-so} = \text{CAS SOC Hamiltonian (e.g. HSO1, HSO2P, HSO2)}$

For SO-MCQDPT, the additional input PARMP defines these matrices differently. For PARMP=0, the spin-free term has diagonal and off-diagonal MCQDPT perturbations:

$H\text{-sf} = \text{CAS-CI spin-free } E + \text{2nd order spin-free MCQDPT}$

$H\text{-so} = \text{CAS SOC Hamiltonian}$

For PARMP not equal to 0, the spin orbit operator is also included into the perturbing Hamiltonian of the MCQDPT:

$H\text{-sf} = \text{CAS-CI spin-free } E + \text{2nd order spin-free MCQDPT}$

$H\text{-so} = \text{CAS SOC Hamiltonian} + \text{2nd order SO-MCQDPT}$

Pure transition moment calculations (OPERAT=DM) are presently limited to CI wavefunctions, so please use only CITYP=GUGA MPLEVL=0. The transition moments computed by SO-MCQDPT runs (see TMOMNT flag) will form the transition density for the CAS-CI zeroth order states rather than the 1st order perturbed wavefunctions.

Please see REFS.DOC for additional information on what is actually a fairly complex input file to prepare.

OPERAT selects the type of transition being computed.

- = DM calculates radiative transition moment between states of same spin, using the dipole moment operator. (default)
- = HSO1 one-electron Spin-Orbit Coupling (SOC)
- = HSO2P partial two electron and full 1e- SOC, namely core-active 2e- contributions are computed, but active-active 2e- terms are ignored. This generally captures >90% of the full HSO2 computation, but with spin-orbit matrix element time similar to the HSO1 calculation.
- = HSO2 one and two-electron SOC, this is the full Pauli-Breit operator.

- = HSO2FF one and two-electron SOC, the form factor method gives the same result as HSO2, but is more efficient in the case of small active spaces, small numbers of CAS-CI states, and large atomic basis sets. This final option applies only to SO-CI.
- PARMP = controls inclusion of the SOC terms in SO-MCQDPT, for OPERAT=HSO1 (default=1) or for HSO2P/HSO2 (default=3) only.
 - 0 - no SOC terms should be included in the MCQDPT corrections at 2nd order, but they will be included in the CAS states on which the MCQDPT (i.e. up to 1st order)
 - 1 - include the 1e- SOC perturbation in MCQDPT
 - 1 - defined under "3", read on...
 - 3 - full 1-electron and partial 2-electron in the form of the mean field perturbation (this is very similar to HSO2P, but in the MCQDPT2 perturbation). Only doubly occupied orbitals (NMODOC) are used for the core 2e contribution. if the option is set to -1, then all core orbitals (NMOFZC+NMODOC) are used. Neither calculation includes extra diagrams including filled orbitals, so both are "partial".

PARMP=3 (or -1) has almost no extra cost compared to PARMP=1, but can only be used with OPERAT=HSO2 or HSO2P. The options -1 and 3 are not rigorously justified, contrary to HOS2P for a SO-CI, as 2e integrals with 2 core indices appear in the second order in two ways. There is a mean- field addition to 1e integrals, which is included when you choose PARMP=3 or -1. But, there are separate terms from additional diagrams that are not implemented, so that there is some imbalance in including the partial 2e correction. Nevertheless, it may be better to include such "partial" partial 2e contributions than not to. Note that at first order in the energy (the CAS-CI states) the N-electron terms are treated exactly as specified by OPERAT.

It is advisable to tighten up the convergence criteria in the \$MCQDx groups since SOC is a fairly small effect, and the spin-free energies should be accurately computed, for example THRCN=1e-8 THRGEN=1e-10.

PARMP has a rather different meaning for OPERAT=HSO2FF: It refers to the difference between ket and bra's Ms,

- 1 do matrix elements for ms=-1 only
- 0 do matrix elements for ms=0 only
- 1 do matrix elements for ms=1 only
- 2 do matrix elements for all ms (0, 1, and -1), which is the default.
- 3 calculates form factors so they can be saved

* * * next defines the orbitals and wavefunctions * * *

- NUMCI = For SO-CI, this parameter tells how many CI calculations to do, and therefore defines how many \$DRTx groups will be read in. For SO-MCQDPT, this parameter tells how many MCQDPT calculations to do, and therefore defines how many \$MCQDx groups will be read in. (default=1) IROOTS, IVEX, NSTATE, and ENGYST below will all have NUMCI values. NUMCI may not exceed 64.

You may wish to define one \$DRTx or \$MCQDx group for each spatial symmetry representation occurring within each spin multiplicity, as the use of symmetry during these separate calculations may make the entire job run much faster.

NUMVEC = the meaning is different depending on the run:

- a) spin-orbit CI (SO-CI), Gives the number of different MO sets. This can be either 1 or 2, but 2 can be chosen only for FORS/CASSCF or FCI wavefunctions. (Default=1) If you set NUMVEC=2 and you use symmetry in any of the \$DRTx groups, you may have to use ISTSYM in the \$DRT groups since the order of orbitals from the corresponding orbital transformation is unpredictable.
- b) spin-orbit perturbation (SO-MCQDPT), The option to have different MOs for different states is not implemented, so your job will have only one \$VEC1 group, and IVEX will not normally be input. The absolute value of NUMVEC should be equal to the value of NUMCI above. If NUMVEC positive, the orbitals in the \$VEC1 will be used exactly as given, whereas if NUMVEC is a negative number, the orbitals will be canonicalized according to IFORB in \$MCQDx. Using NUMVEC=-NUMCI and IFORB=3 in all \$MCQDx to canonicalize over all states is recommended.

Note that \$GUESS is not read by this RUNTYP! Orbitals must be in \$VEC1 and possibly \$VEC2 input groups.

NFZC = For SO-CI, this is equal to NFZC in each \$DRTx group. When NUMVEC=2, this is also the number of identical core orbitals in the two vector sets. For SO-MCQDPT, this should be NMOFZC+NMODOC given in each of the \$MCQDx groups. The default is the number of AOs given in \$DATA, this is not very reasonable.

NOCC = the number of occupied orbitals. For SO-CI this should be NFZC+NDOC+NALP+NAOS+NBOS+NVAL, but add the external orbitals if the CAS-CI states are CI-SD or FO CI or SOCI type instead of CAS. For SO-MCQDPT enter NUMFZC+NUMDOC+NUMACT. The default is the number of AOs given in \$DATA, which is not usually correct.

Note: IROOTS, NSTATE, ENGYST, IVEX contain NUMCI values.

IROOTS = array containing the number of CAS-CI states to be used from each CI or MCQDPT calculation. The default is 1 for every calculation, which is probably not a correct choice for OPERAT=DM runs, but is quite reasonable for the HSO operators. The total number of states included in the SOC Hamiltonian is the summation of the NUMCI values of IROOTS times the multiplicity of each CI or MCQDPT. See also ETOL.

NSTATE = array containing the number of CAS-CI states to be found by diagonalising the spin-free Hamiltonians. Of these, the first IROOTS(i) states will be used to find transition moments or SOC. Obviously, enter NSTATE(i) >= IROOTS(i). The default for NSTATE(i) is IROOTS(i), but might be bigger if you are curious about the additional energies, or to help the Davidson diagonalizer. NSTATE is ignored by SO-MCQDPT runs, and you must ensure that your IROOTS input corresponds to the KSTATE option in \$MCQDx.

ETOL = energy tolerance for CI state elimination. This applies only to SO-CI and OPERAT=HSO1,2,2P. After each CI finds NSTATE(i) CI roots for each \$DRTx, the number of states kept in the run is normally IROOTS(i), but ETOL applies the further constraint that the states kept be within ETOL of

the lowest energy found for any of the \$DRTx. The default is 100.0 Hartree, so that IROOTS is the only limitation.

- IVEX = Array of indices of \$VECX groups to be used for each CI calculation. The default for NUMVEC=2 is IVEX(1)=1,2,1,1,1,1,1..., and of course for NUMVEC=1, it is IVEX(1)=1,1,1,1,1... This applies only to CITYP=GUGA jobs.
- ENGYST = energy values to replace the CI spin-free energies. This parameter applies to SO-CI only. A possible use for this is to use first or second order CI energies (FOCI or SOCI in \$DRT) on the diagonal of the Hamiltonian (obtained in some earlier runs) but to use only CAS wavefunctions to evaluate off diagonal HSO matrix elements. The CAS-CI runs are still conducted to obtain CI coefs, needed to evaluate the off diagonal elements. Enter MXRT*NUMCI values as a square array, by the usual FORTRAN convention (that is, MXRT roots of \$DRT1, MXRT roots of \$DRT2 etc), in hartrees, with zeros added to fill each column to MXRT values. MXRT is the maximum value in the IROOTS array. (the default is the computed CAS-CI energies) See B.Schimmelpfennig, L.Maron, U.Wahlgren, C.Teichtel, H.Fagerli, O.Gropen Chem.Phys.Lett. 286, 261-266(1998).

* * * the next pertain only to spin-orbit runs * * *

- RSTATE = sets the zero energy level format: ndrt*1000+iroot for adiabatic state (CI root)
0000 sets zero energy to the lowest diabatic root
default: 1001 (1st root in \$DRT1 or \$MCQD1)
- ZEFTYP specifies effective nuclear charges to use.
- = TRUE uses true nuclear charge of each atom, except protons are removed if an ECP basis is being used (default).
 - = 3-21G selects values optimized for the 3-21G basis, but these are probably appropriate for any all electron basis set. Rare gases, transition metals, and Z>54 will use the true nuclear charges.
 - = SBKJC selects a set obtained for the SBKJC ECP basis set, specifically. It may not be sensible to use these for other ECP sets. Rare gases, lanthanides, and Z>86 will use the true nuclear charges.
- ZEFF = an array of effective nuclear charges, overriding the charges chosen in ZEFTYP.

Note that effective nuclear charges can be used for any HSO type OPERAT, but traditionally these are used mainly for HSO1 as an empirical correction to the omission of the 2e- term, or to compensate for missing core orbitals in ECP runs.

- JZ controls the calculation of Jz eigenvalues
- = 0 do not perform the calculation
 - = 1 do the calculation
- By default, Jz is set to 1 for molecules that are recognised as linear (this

includes atoms!). Jz cannot be computed for nonlinear molecules. The matrix of $J_z = L_z + S_z$ operator is constructed between spin-mixed states (eigenvalues of Hso). Setting Jz to 1 can enforce otherwise avoided (by symmetry) calculations of SOC matrix elements. JZ applies only to HSO1,2,2P.

- TMOMNT = flag to control computation of the transition dipole moment between spin-mixed wavefunctions (that is, between eigenvectors of the Pauli-Breit Hamiltonian). Applies only to HSO1,2,2P. (default is .FALSE.)
- SKIPDM = flag to omit(.TRUE.) or include(.FALSE.) dipole moment matrix elements during spin-orbit coupling. Usually it takes almost no addition effort to calculate $\langle R \rangle$ excluding some cases when the calculation of forbidden by symmetry spin-orbit coupling matrix elements $\langle H_{so} \rangle$ may have to be performed since $\langle R \rangle$ and $\langle H_{so} \rangle$ are computed simultaneously. Applies only to HSO1,2,2P. Since the lack of a MCQDPT density matrix means there are no MCQDPT dipole moments at present, SO-MCQDPT jobs will compute the dipole matrix elements for the CAS-CI states only. However, the dipole moments in the spin-mixed states will be computed with the MCQDPT mixing coefficients. (default is .TRUE.)
- IPRHSO = controls output style for matrix elements (HSO*)
 = -1 do not output individual matrix elements otherwise these are accumulative:
 = 0 term-symbol like kind of labelling: labels contain full symmetry info (default)
 = 1 all states are numbered consequently within each spin multiplicity (ye olde style)
 = 2 output only nonzero ($\geq 1e-4$) matrix elements
- PRTPRM = flag to provide detailed information about the composition of the spin-mixed states in terms of adiabatic states. This flag also provides similar information about Jz (if JZ set). (default is .FALSE.)

* * * expert mode HSO control options * * *

- MODPAR = parallel options, which are independent bit options, 0=off, 1=on. Bit 1 refers only to HSO2FF, bit 2 to HSO1,2,2P. Enter a decimal value 0, 1, 2, 3 meaning binary 00, 01, 10, 11.
- bit 1 = 0/1 (HSO2FF) uses static/dynamic load balancing in parallel if available, otherwise use static load balancing. Dynamic algorithm is usually faster but may utilize memory less efficiently, and I/O can slow it down. Also, dynamical algorithm forces SAVDSK=.F. since its unique distribution of FFs among nodes implies no savings from precalculating form factors.
- bit 2 = 0/1 (HSO1,2,2P) duplicate/distribute SOC integrals in parallel. If set, 2e AO integrals and the four-index transformation are divided over nodes (distributed), and SOC MO integrals are then summed over nodes.
- The default is 3, meaning both bits are set on (11)

- PHYSRC = flag to force the size of the physical record to be equal to the size of the sorting buffers. This option can have a dramatic effect on the efficiency.

Usually, setting PHYSRC=.t. is helpful if the code complains that low memory enforces SLOWFF=.TRUE., or you set it yourself. For large active spaces and large memory (more precisely, if reclen is larger than the physical record size) PHYSRC=.TRUE. can slow the code down. Setting PHYSRC to .true. forces SLOWFF to be .false. See MODPAR. (default .FALSE.) (only with HSO2FF)

RECLEN = specifies the size of the record on file 40, where form factors are stored. This parameter significantly affects performance. If not specified, RECLEN have to be guessed, and the guess will usually be either an overestimate or underestimate. If the former you waste disk space, if the latter the program aborts. Note that RECLEN will be different for each pair of multiplicities and you must specify the maximum for all pairs. The meaning of this number is how many non-zero form factors are present given four MO indices. You can decrease RECLEN if you are getting a message "predicted sorting buffer length is greater than needed..." Default depends on active space. (only HSO2FF)

SAVDSK = flag to repeat the form factor calculation twice. This avoids wasting disk space as the actually required record size is found during the 1st run. (default=.FALSE.) (only with HSO2FF)

SLOWFF = flag to choose a slower FF write-out method. By default .FALSE., but this is turned on if:

- 1) not enough memory for the fast way is available
- 2) the maximum usable memory is available, as when the buffer is as large as the maximum needed, then the "slow FF" algorythm is faster.

Generally SLOWFF=.true. saves up to 50% or so of disk space. See PHYSRC. (only with HSO2FF)

ACTION controls disk file DAFL30 reuse.

- = NORMAL calculate the form factors in this run.
- = SAVE calculate, and store the form factors on disk for future runs with the same active space characteristics.
- = READ read the form factors from disk from an earlier run which used SAVE. (default=NORMAL) (only with HSO2FF)

Note that currently in order to use ACTION = SAVE or READ you should specify MS= -1, 0, or 1

* * * some control tolerances * * *

NOSYM = -1 forces use of symmetry-contaminated orbitals symmetry analysis, otherwise the same as NOSYM=0

- = 0 fully use symmetry
- = 1 do not use point group symmetry, but still use other symmetries (Hermiticity, spin).
- = 2 use no symmetry. Also, include all CSFs for HSO1, 2, 2P.
- = 3 force the code to assume the symmetry specified in \$DATA is the same as in all \$DRT groups, but is otherwise identical to NOSYM=-1. This option saves CPU time and money(memory). Since the \$DRT works by mapping non-Abelian groups into their highest Abelian subgroup, do not use NOSYM=3 for non-Abelian groups.

SYMTOL = relative error for the matrix elements. This parameter has a great impact upon CPU time, and the default has been chosen to obtain nearly full accuracy while still getting good speedups. (default=1.0E-4)

* * * the remaining parameters are not so important * * *

PRTCMO = flag to control printout of the corresponding orbitals. (default is .FALSE.)

HSOTOL = HSO matrix elements are considered zero if they are smaller than HSOTOL. This parameter is used only for print-out and statistics. (default=1.0E-1 cm⁻¹)

TOLZ = MO coefficient zero tolerance (as for \$GUESS). (default=1.0E-8)

TOLE = MO coefficient equating tolerance (as for \$GUESS). (default=1.0E-5)

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For information on RUNTYP=TRANSITN, see the 'further information' section

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